X-Ray Studies of Diffusion Dynamics in Nano-Confined Geometries

THE BEST THESIS DEFENSE IS A GOOD THESIS OFFENSE.

Leandra Boucheron • Dissertation Defense • October 8, 2015

Outline

- Introduction
- Techniques
  - Langmuir-Blodgett Films
  - X-Ray Photon Correlation Spectroscopy (XPCS)
- Results
  - Non-Equilibrium Dynamics
  - Aging
  - Jamming Transition
- Conclusion

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Introduction

You do not really understand something unless you can explain it to your grandmother.

Leandra, a lot of things are nanotechnology. Tennis balls are nanotechnology. Even *humans* are nanotechnology!

If you really understand something, you can afford to explain it using language that can be easily understood.

Ongoing process

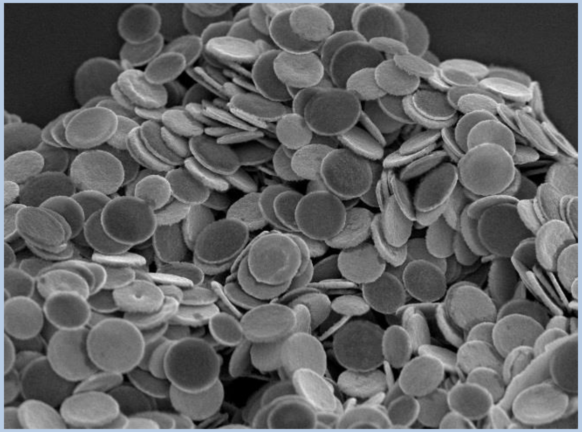
Ways to Look at Small Things

Optical Microscopy
>100nm

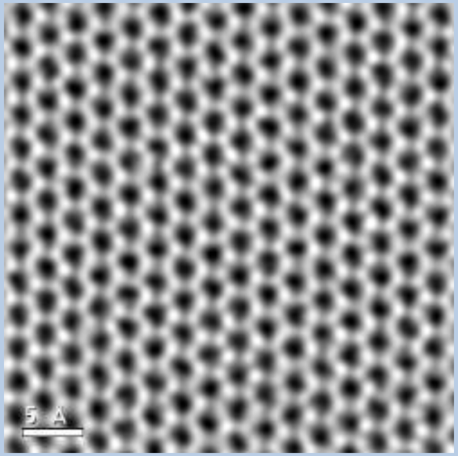
Diffraction Limit

$$d \sim \lambda$$

Scanning Electron Microscopy
>1nm



Transmission Electron Microscopy
>1Å

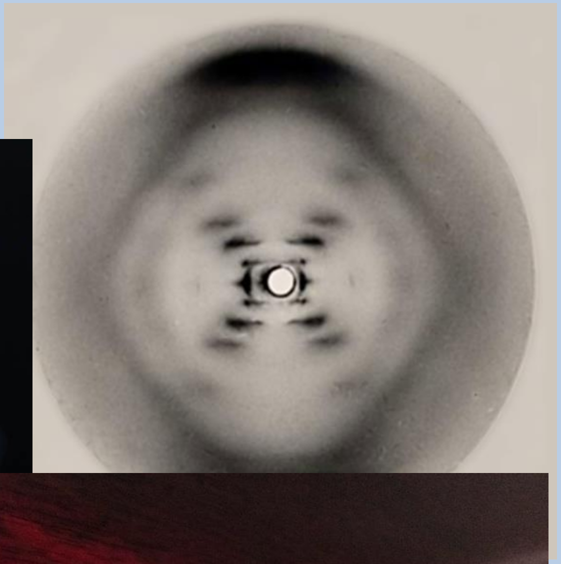


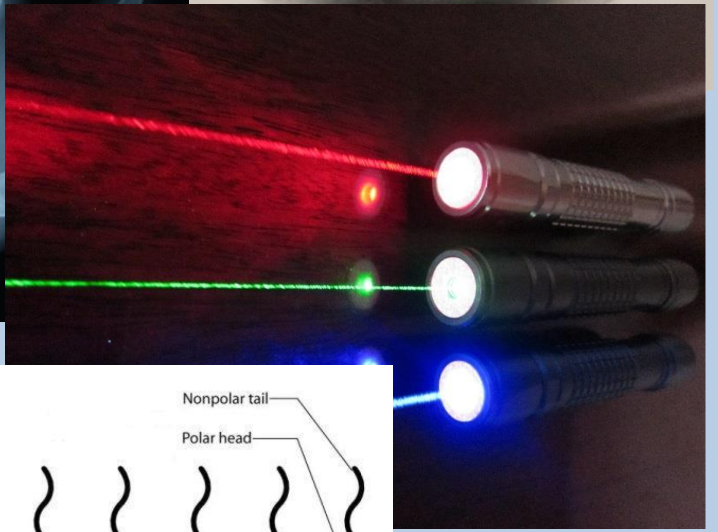
De Broglie Wavelength

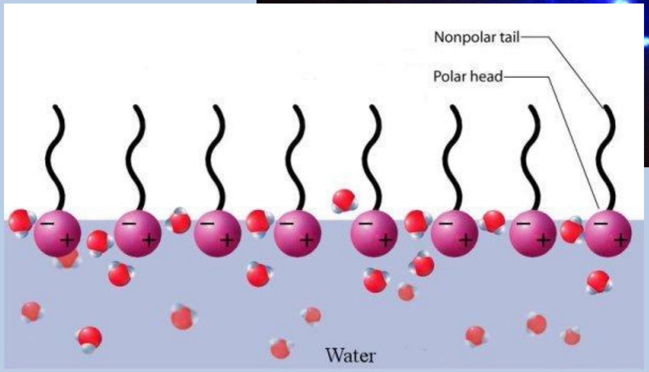
$$\lambda = \frac{h}{p}$$

Why X-Rays?

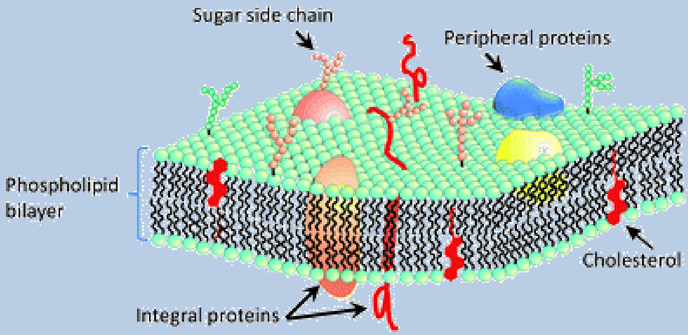
- Wavelength (10pm-10nm)
- Penetrating
- Non-Invasive
- **Global, Statistical Information**
- *In situ* Studies
- Surface Sensitivity (GID)
- Coherence (XPCS)



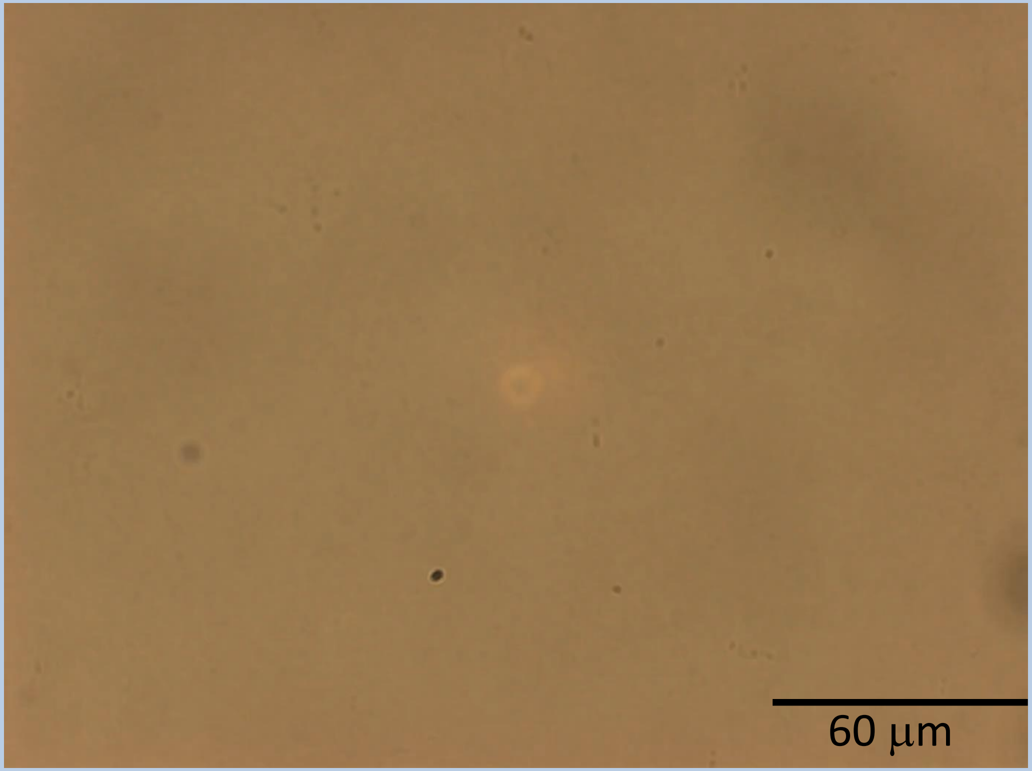




Interfacial Structures (Thin Films)



10nm iron oxide nanoparticle film during compression on liquid surface



How do individual particle dynamics affect the film structure?

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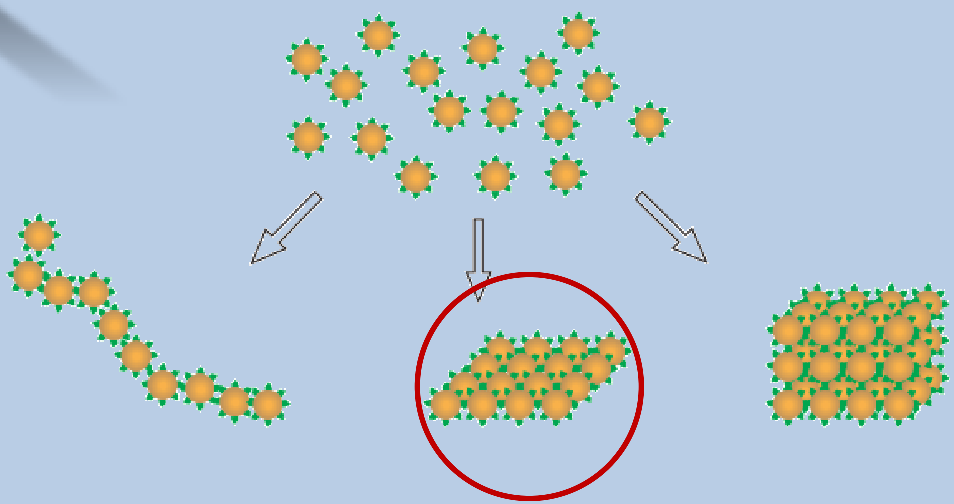
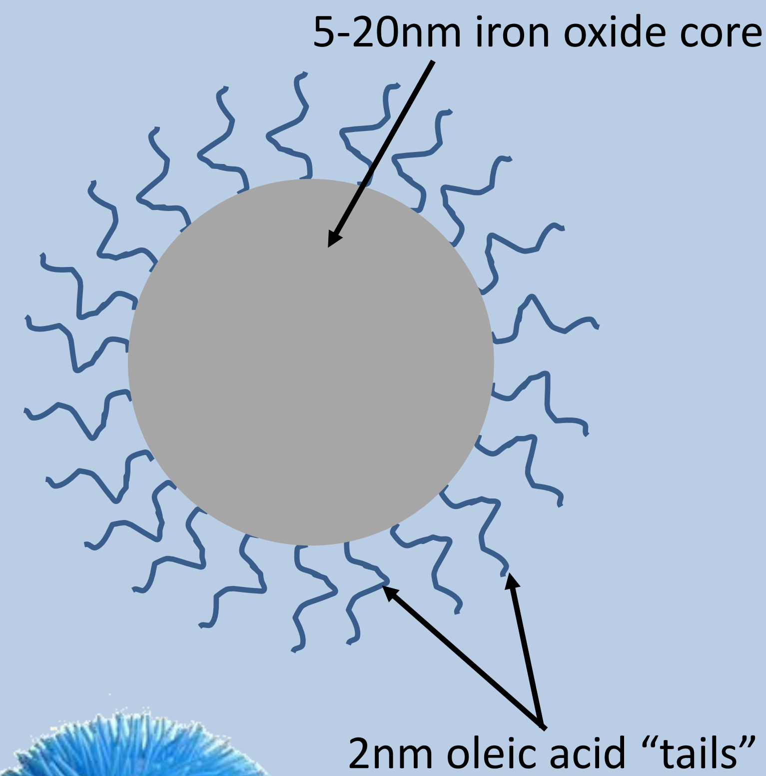
Liquid Surface Self Assembly

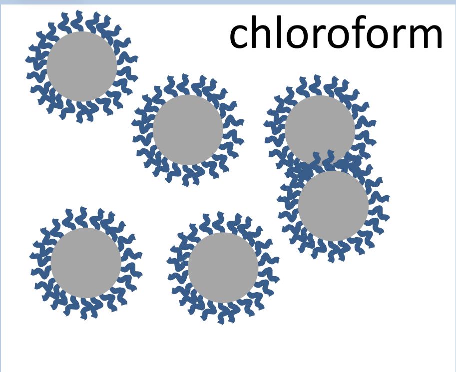


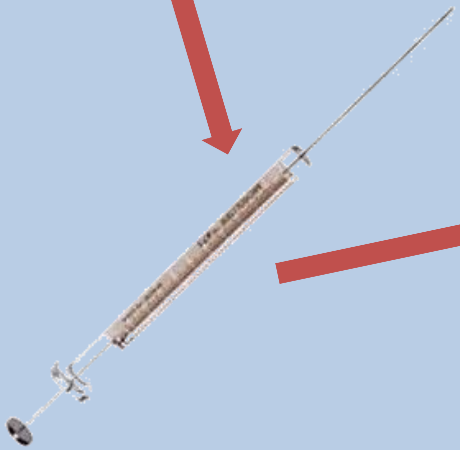


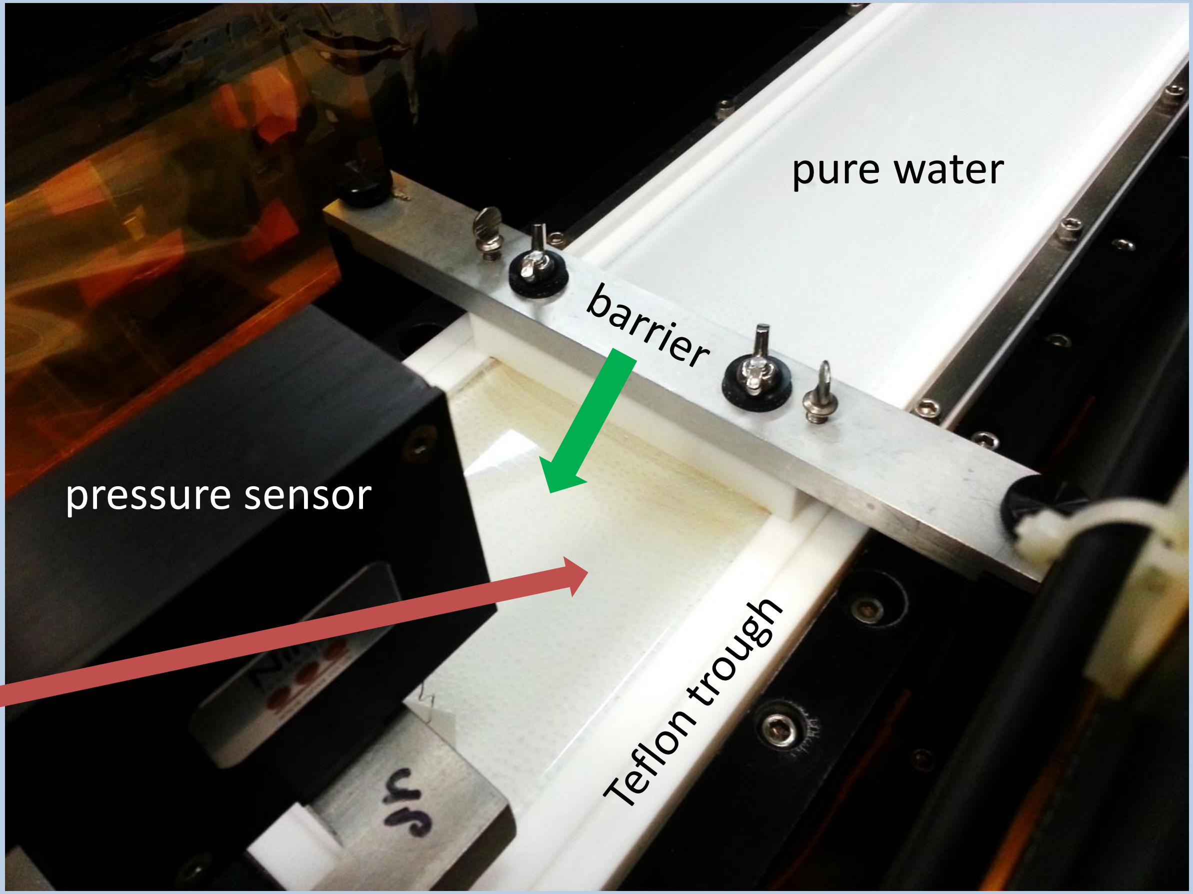
- Van der Waals Force
- Interfacial Forces
- Magnetic Interactions
- Electric Interactions

Nie, Z., Petukhova, A., & Kumacheva, E. (2010). *Nature nanotechnology*, *5*(1)

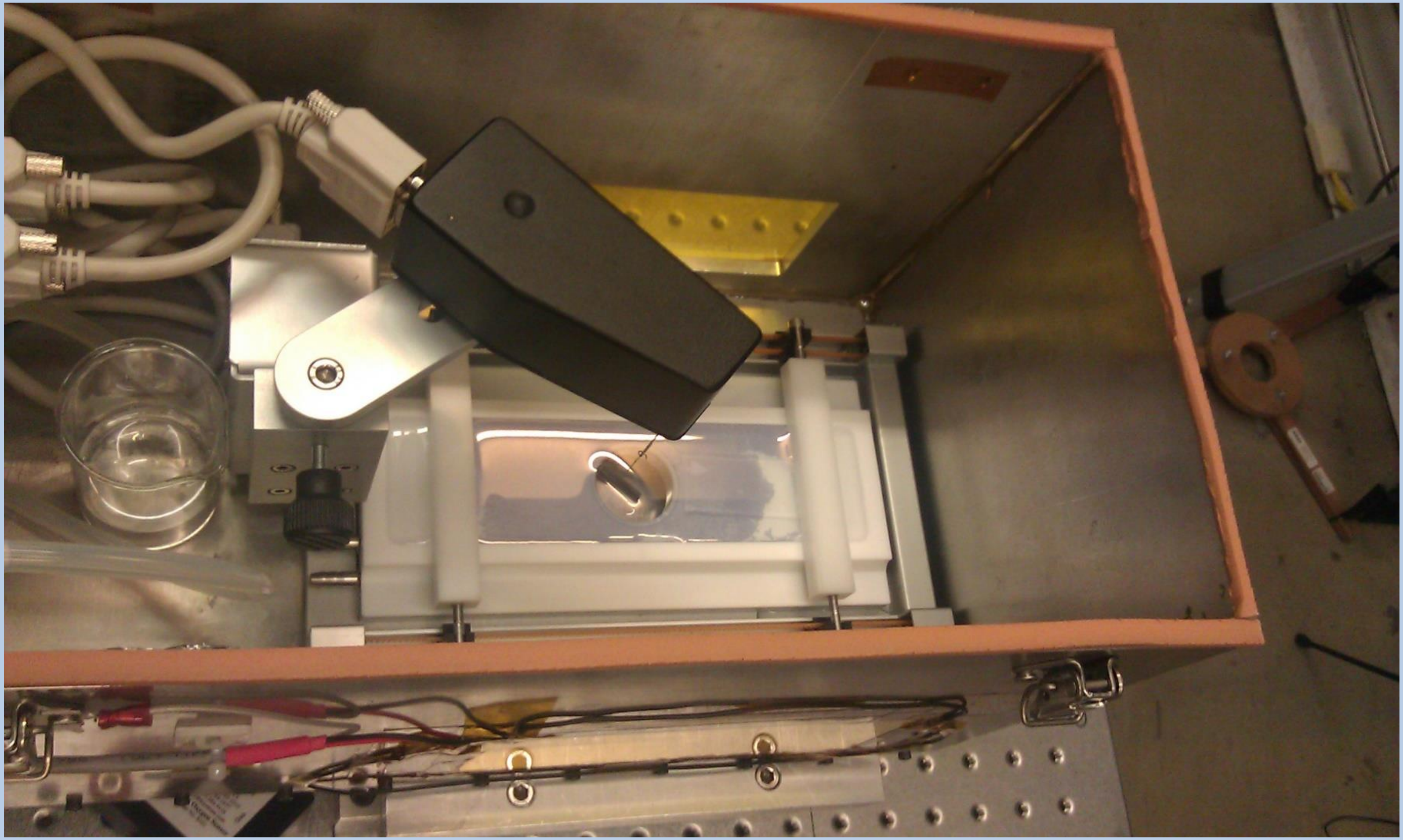
Langmuir-Blodgett Trough







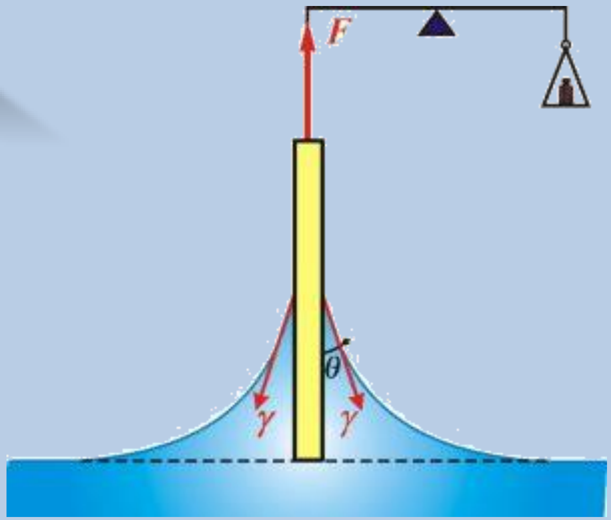
Monolayers

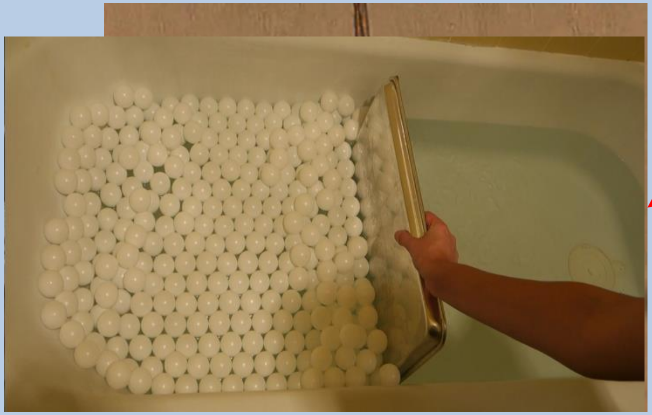


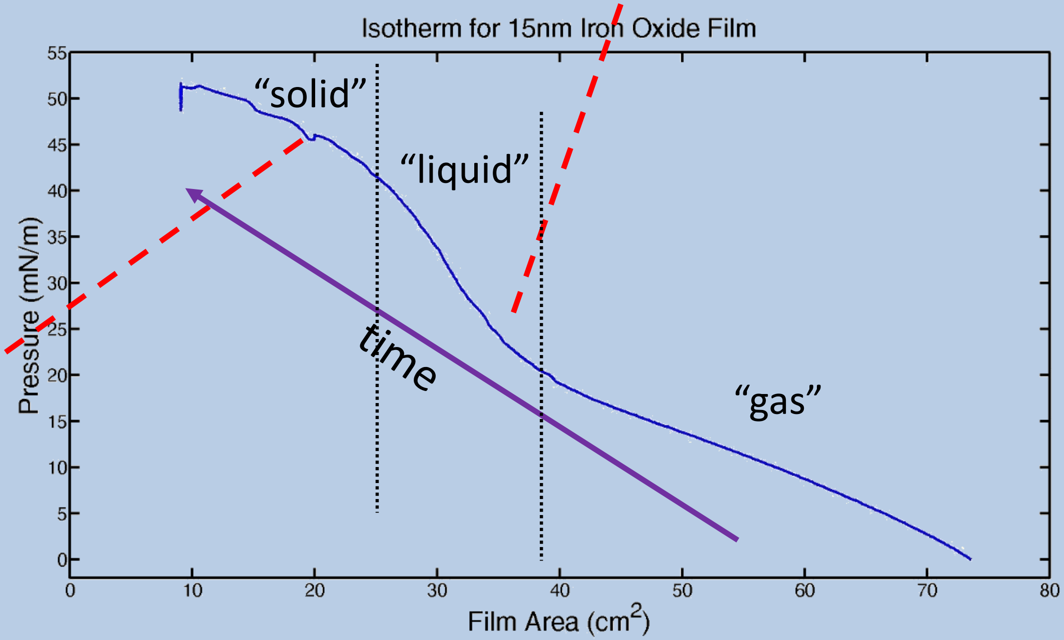
Macroscale Self-Assembly (Cheerios Effect)

Macroscale Compression

Isotherms

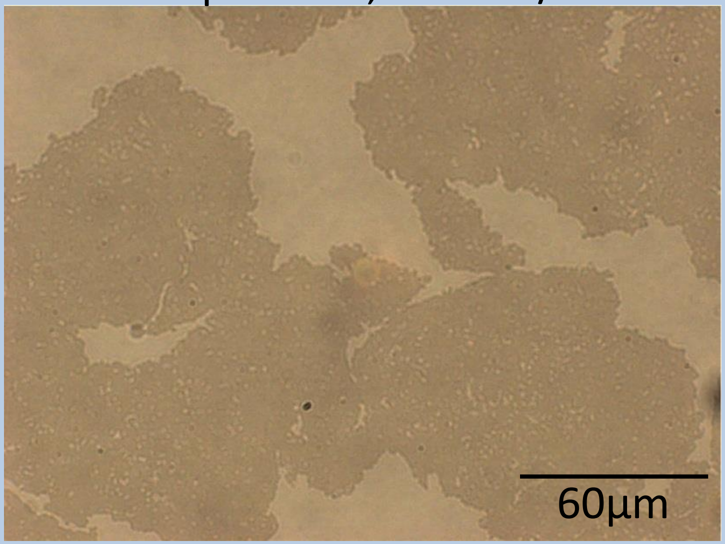

F
θ
γ
γ



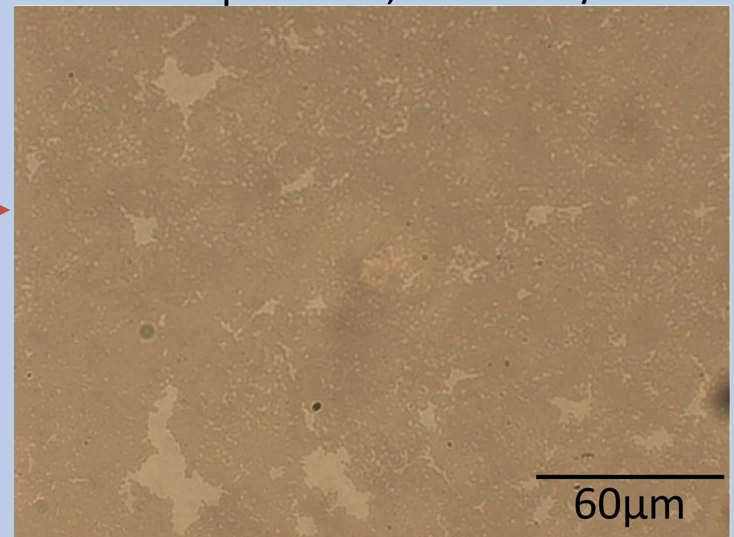

Isotherm for 15nm Iron Oxide Film
"solid"
"liquid"
"gas"
time
Pressure (mN/m)
Film Area (cm^2)
0
5
10
15
20
25
30
35
40
45
50
55
0
10
20
30
40
50
60
70
80

The Microscopic Picture

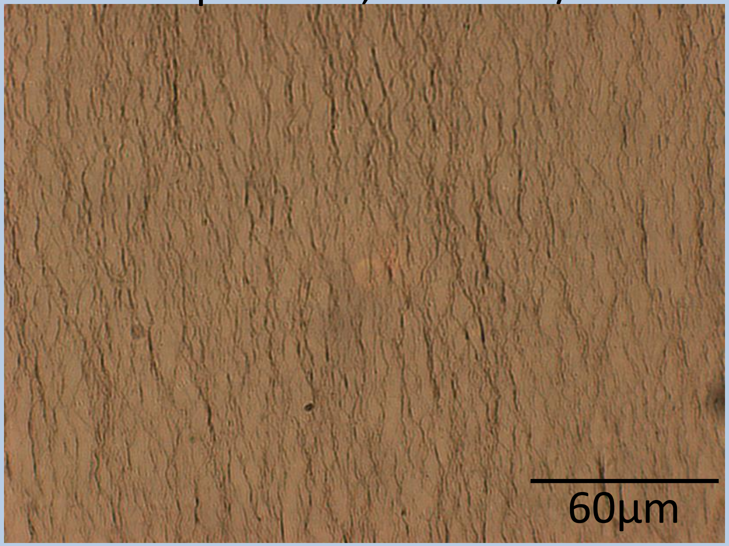
20nm particles, Π~5mN/m



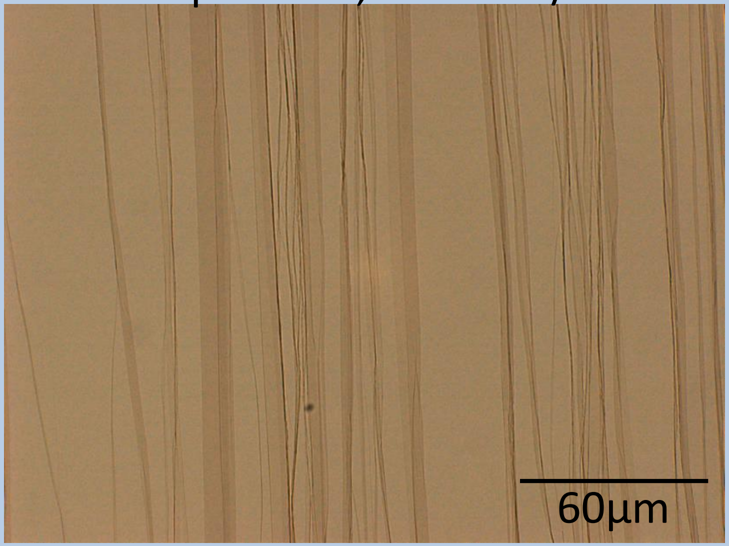
20nm particles, Π~15mN/m



20nm particles, Π~40mN/m



5nm particles, Π~40mN/m



The Nanoscopic Picture

???

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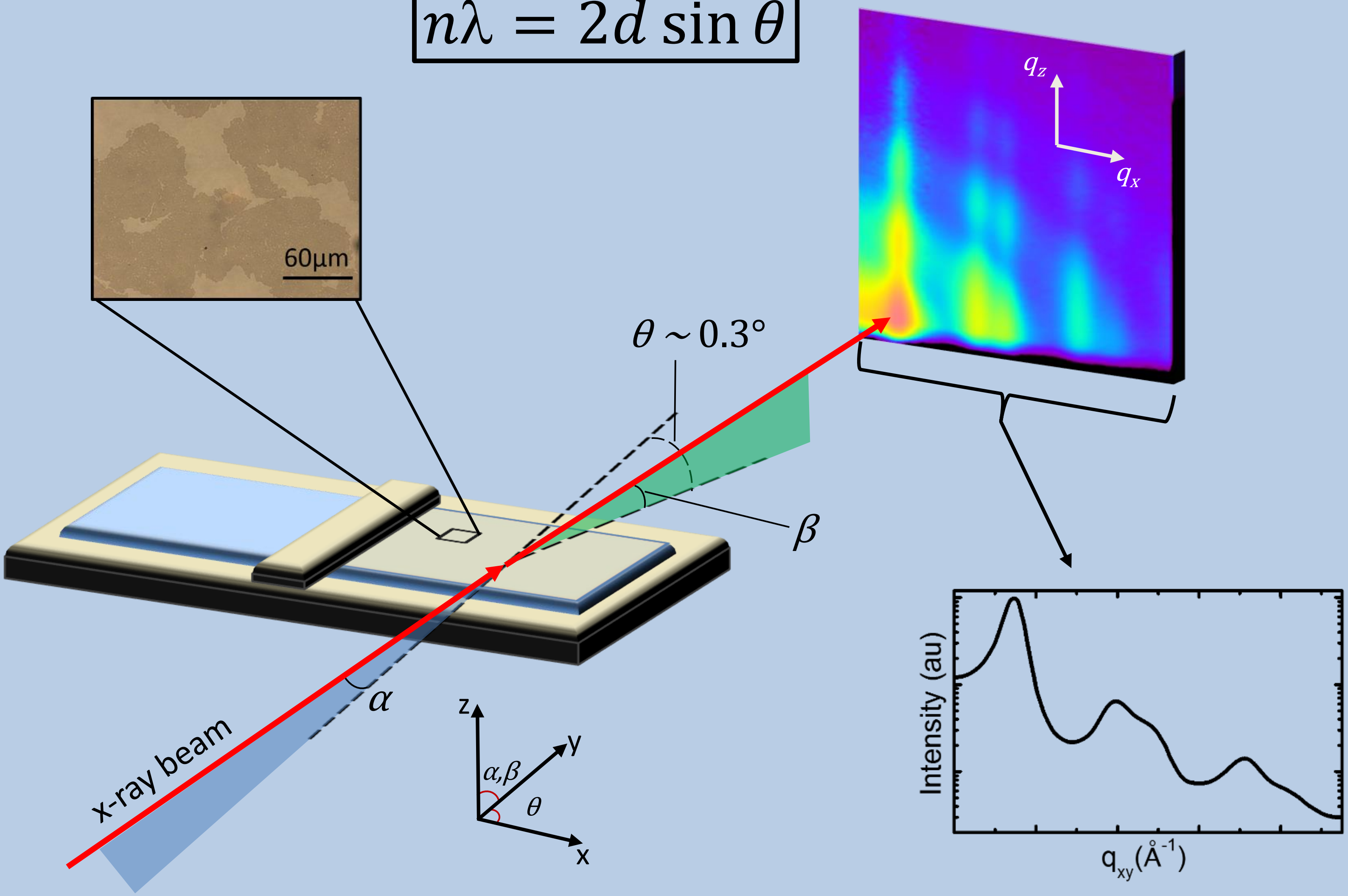
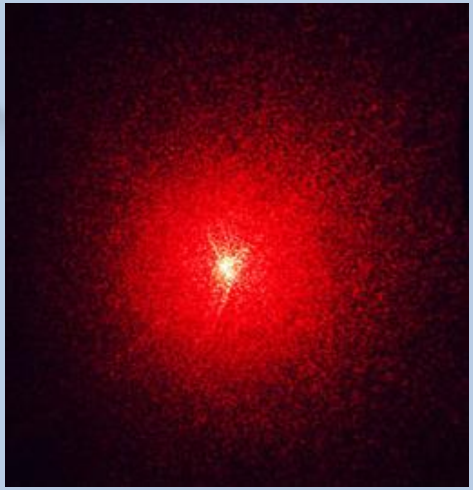
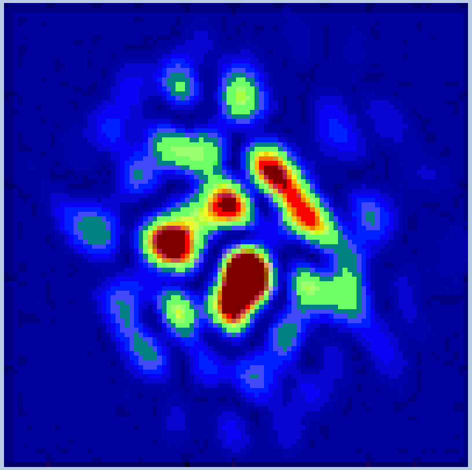
Grazing Incidence Diffraction (GID)

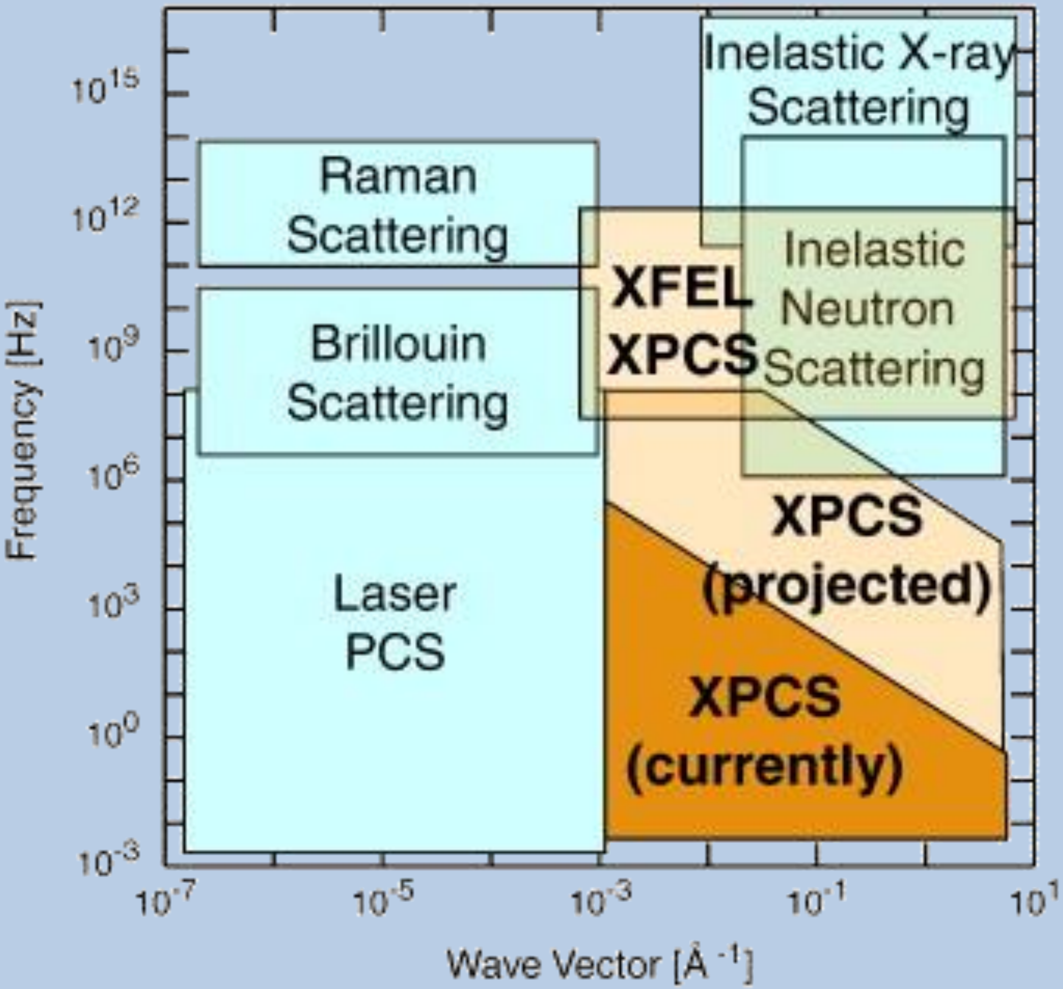
$$n\lambda = 2d \sin\theta$$



Coherent Speckle





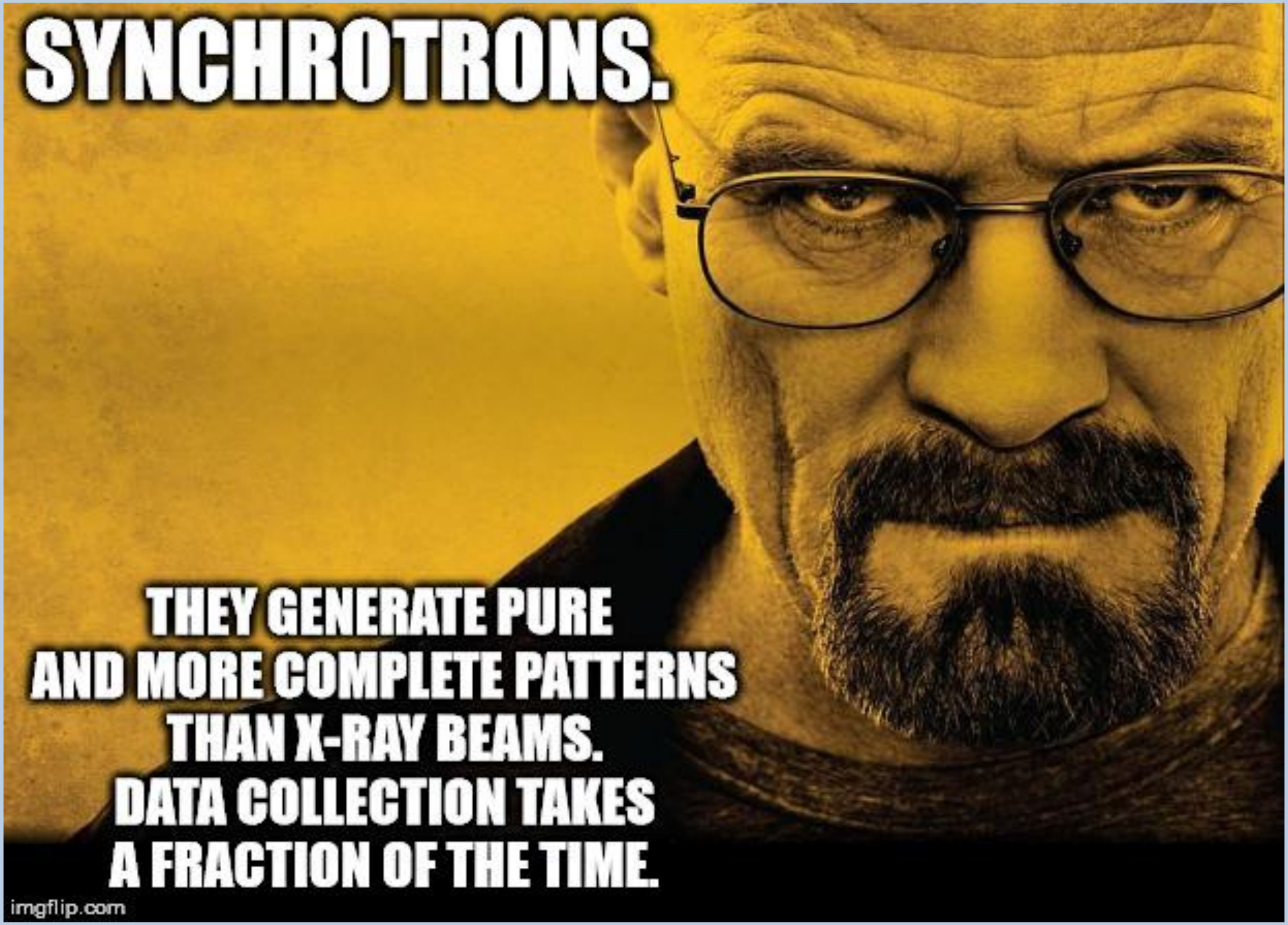


Leheny, R.L. (2012). *Current Opinion in Colloid & Interface Science*, *17*(1)

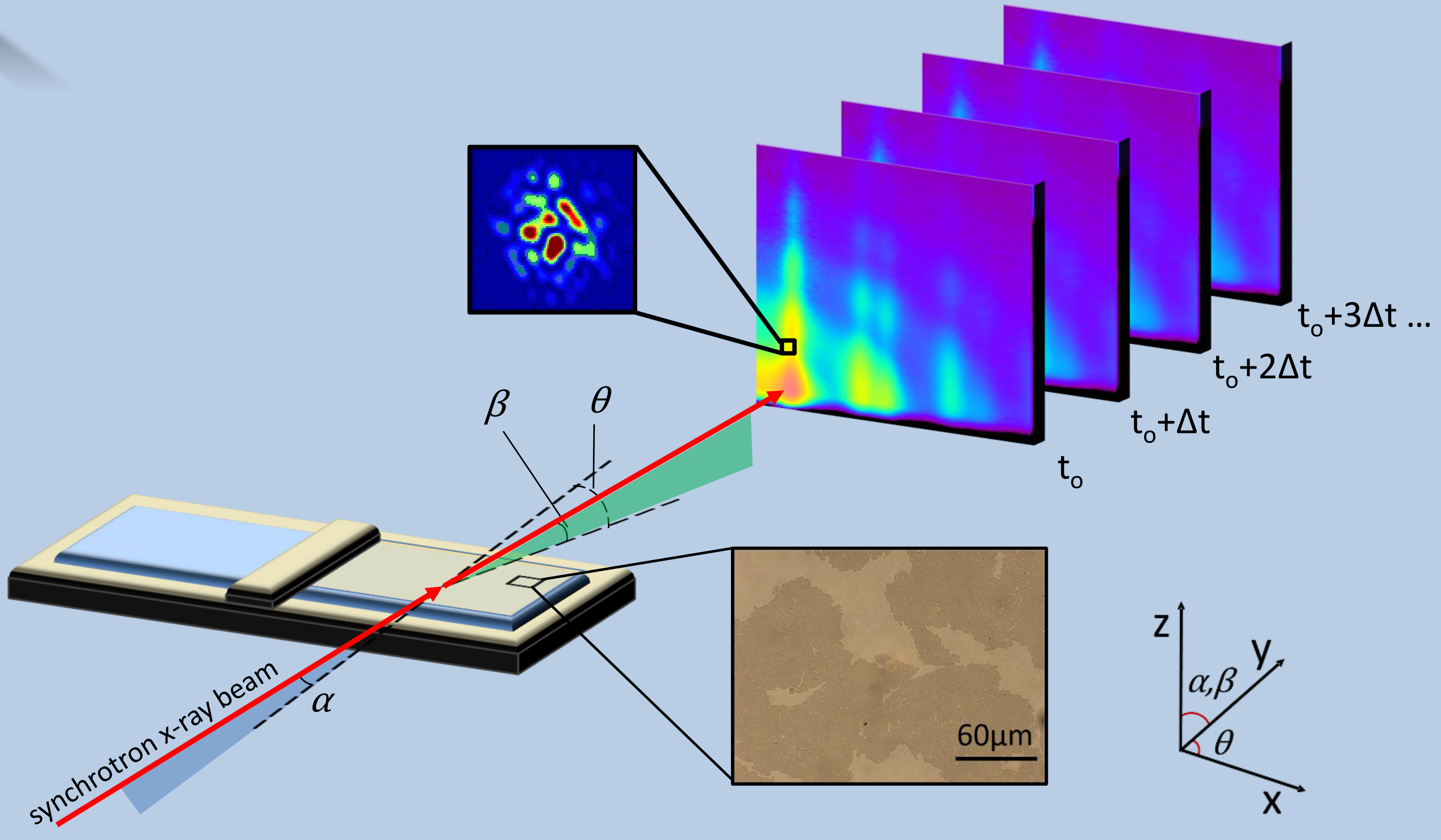
Experimental Location

Advanced
Photon
Source
Argonne National Laboratory

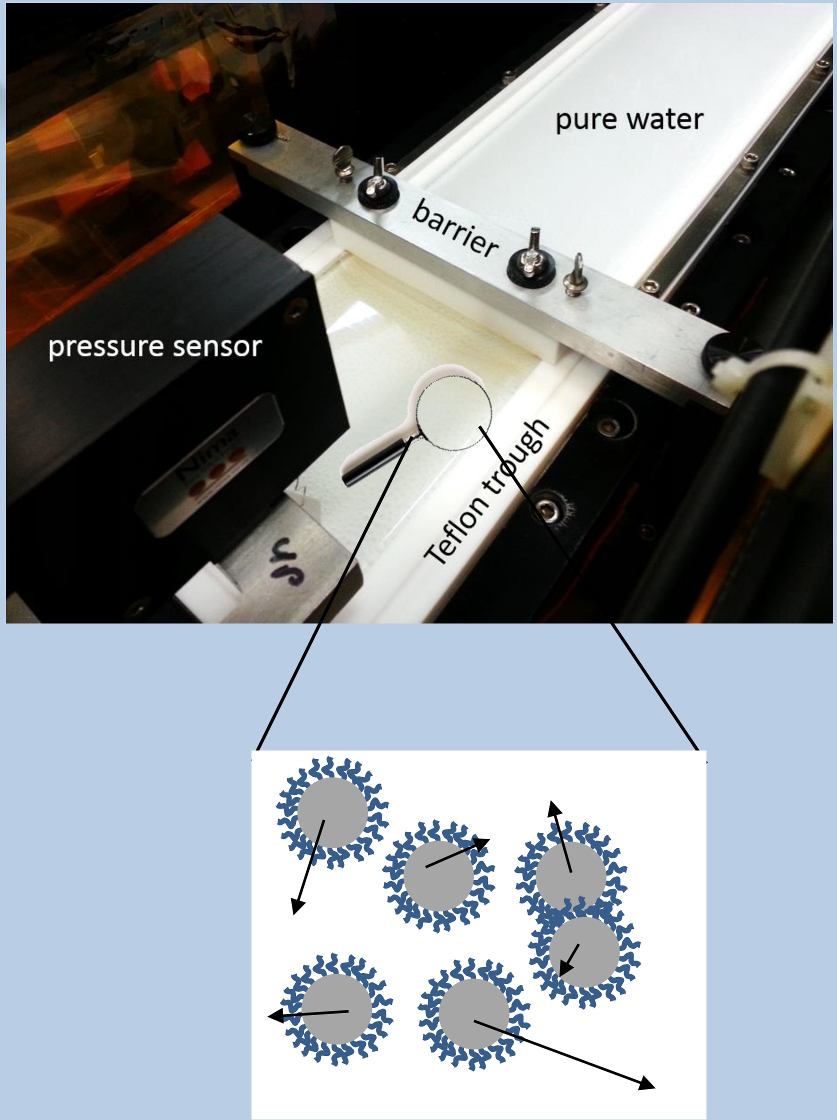
Experimental Justification



X-Ray Photon Correlation Spectroscopy (XPCS)



Timescales

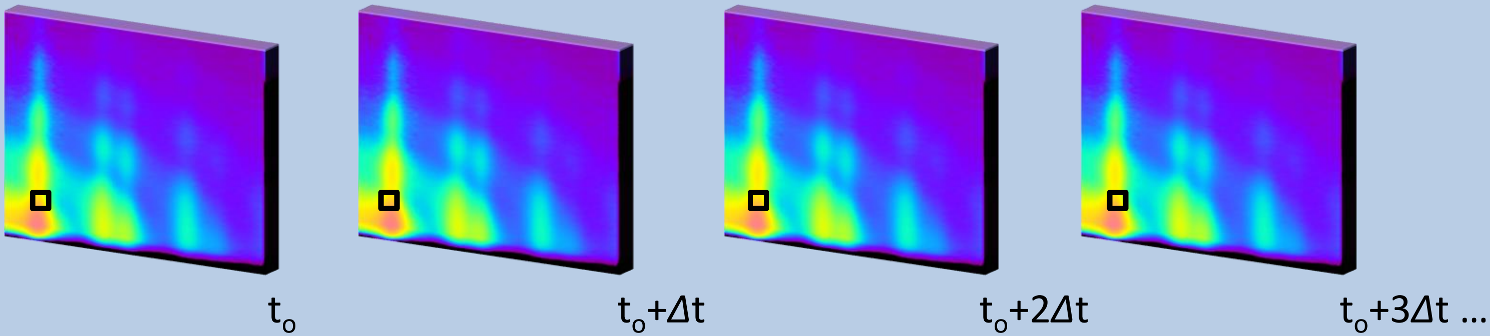


How *old* is the film? (age) - hours

How *quickly* are the particles moving? (dynamics timescale) – hundreds of seconds (τ)

Experimental Setup

Interparticle Dynamics



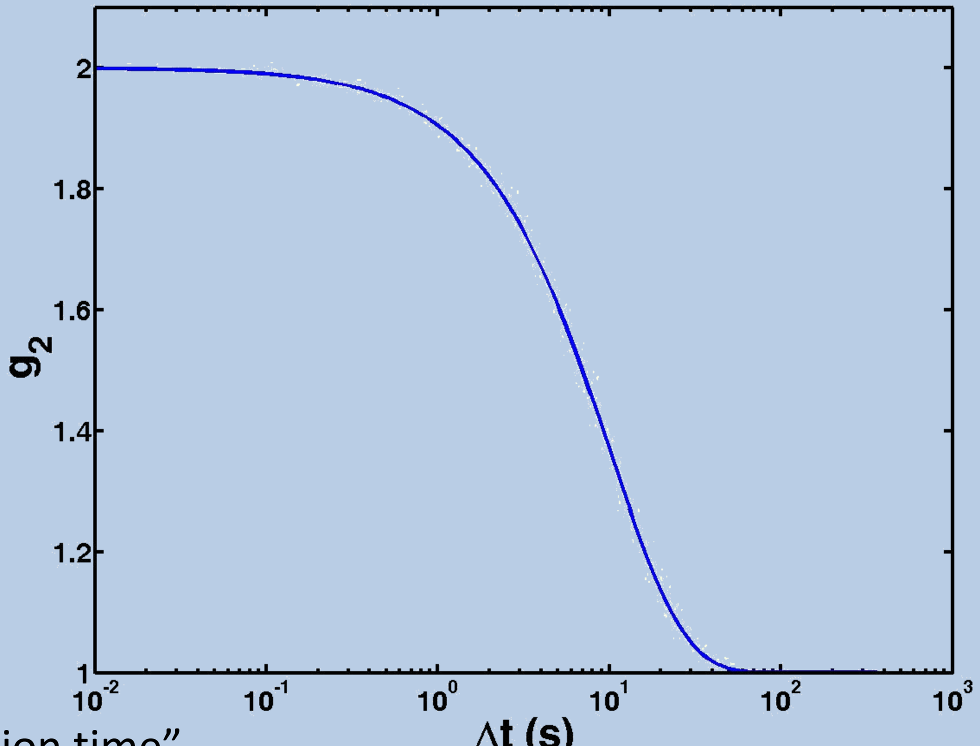
$$g_2(\Delta t) = \frac{\langle I(t) I(t+\Delta t)\rangle_t}{\langle I(t)\rangle_t{}^2}$$

No motion – constant intensity

Motion – changing intensity, decorrelation

$$g_2(\Delta t) - 1 = b\left[Ae^{-\left(\frac{t}{\tau}\right)^{\beta}}\right]^2$$

$\beta = 1$ (here)



τ = "characteristic timescale" or "relaxation time"

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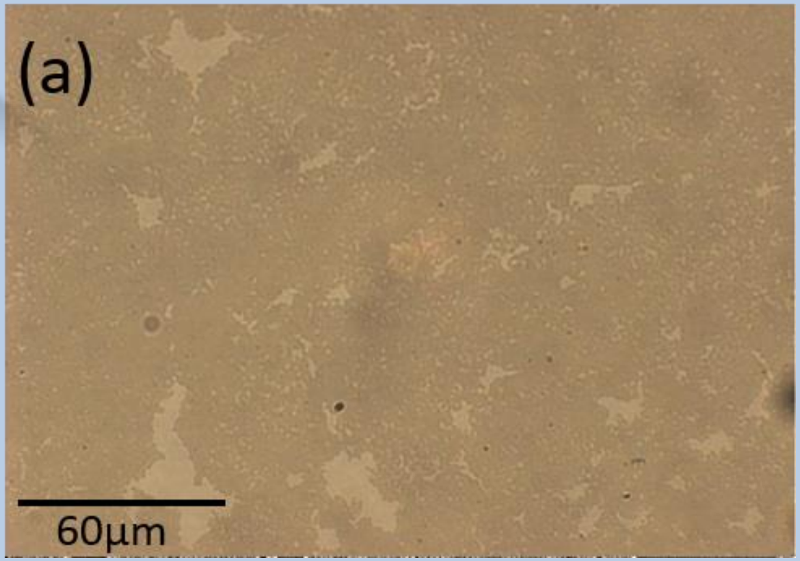
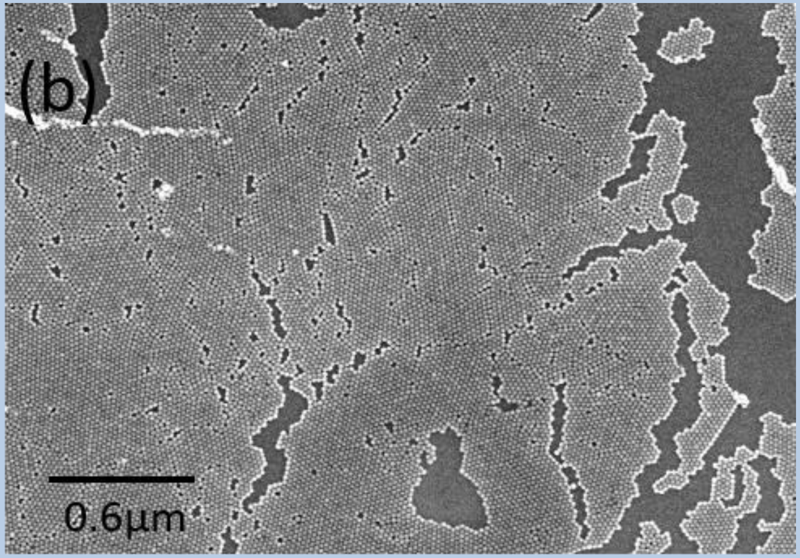
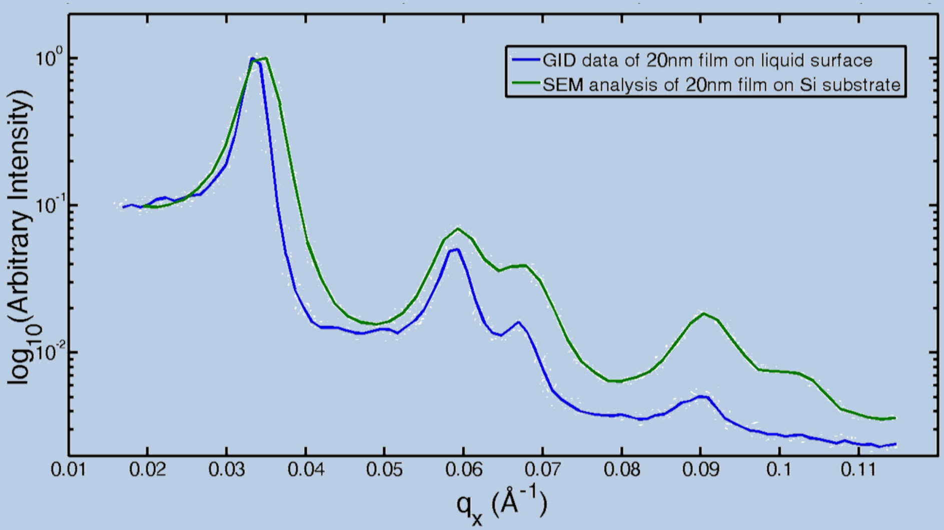
Nanoscale Grain Boundaries

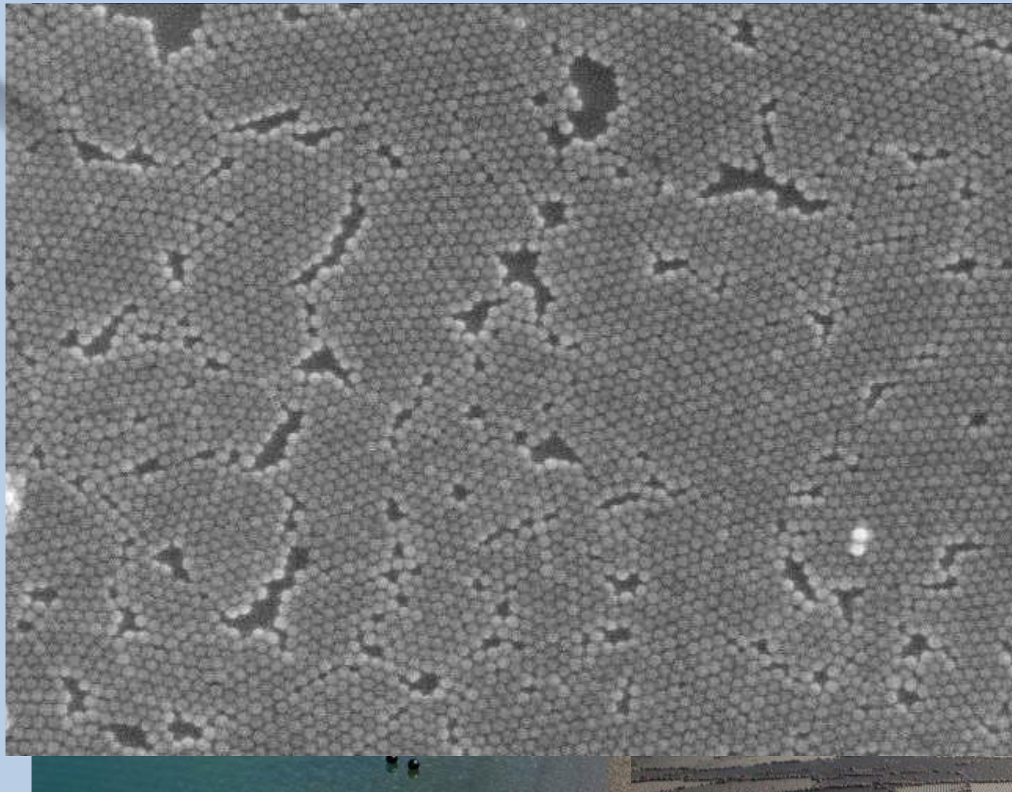


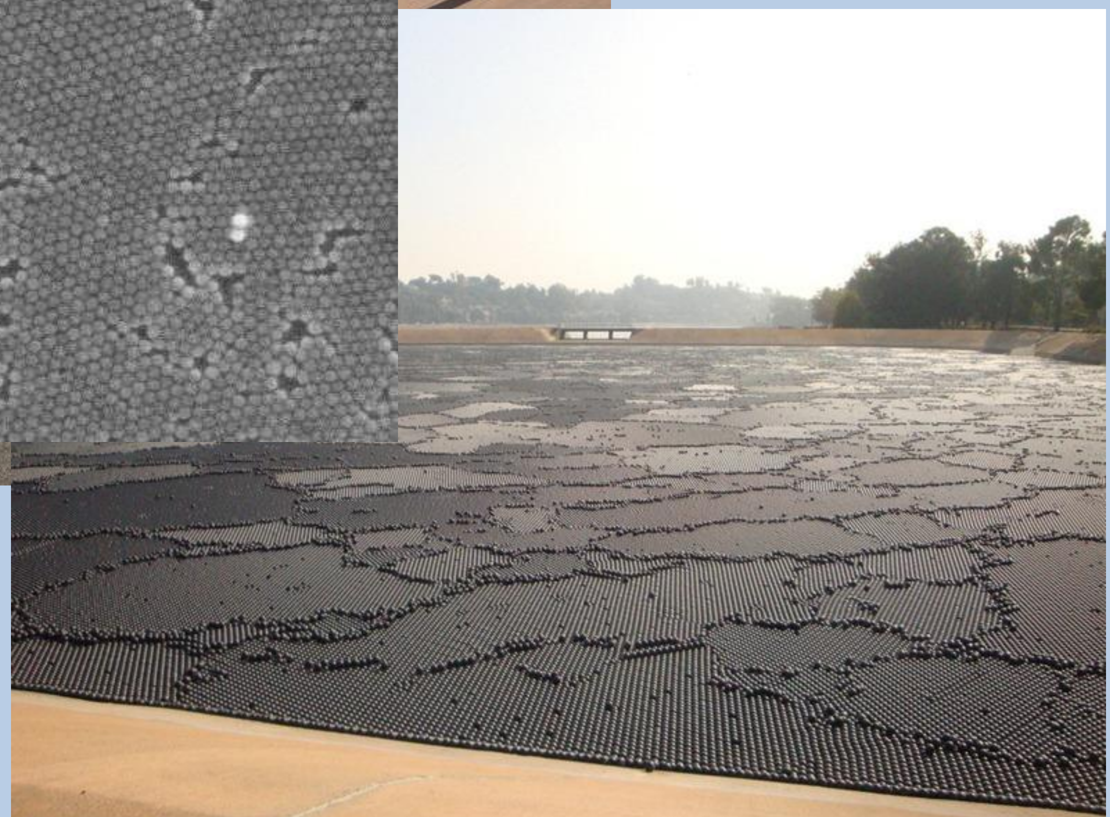




Stanley, J., et. al. *Rev. Sci. Instrum*. 86, 063704 (2015);

Macroscale Grain Boundaries





Experimental Procedure

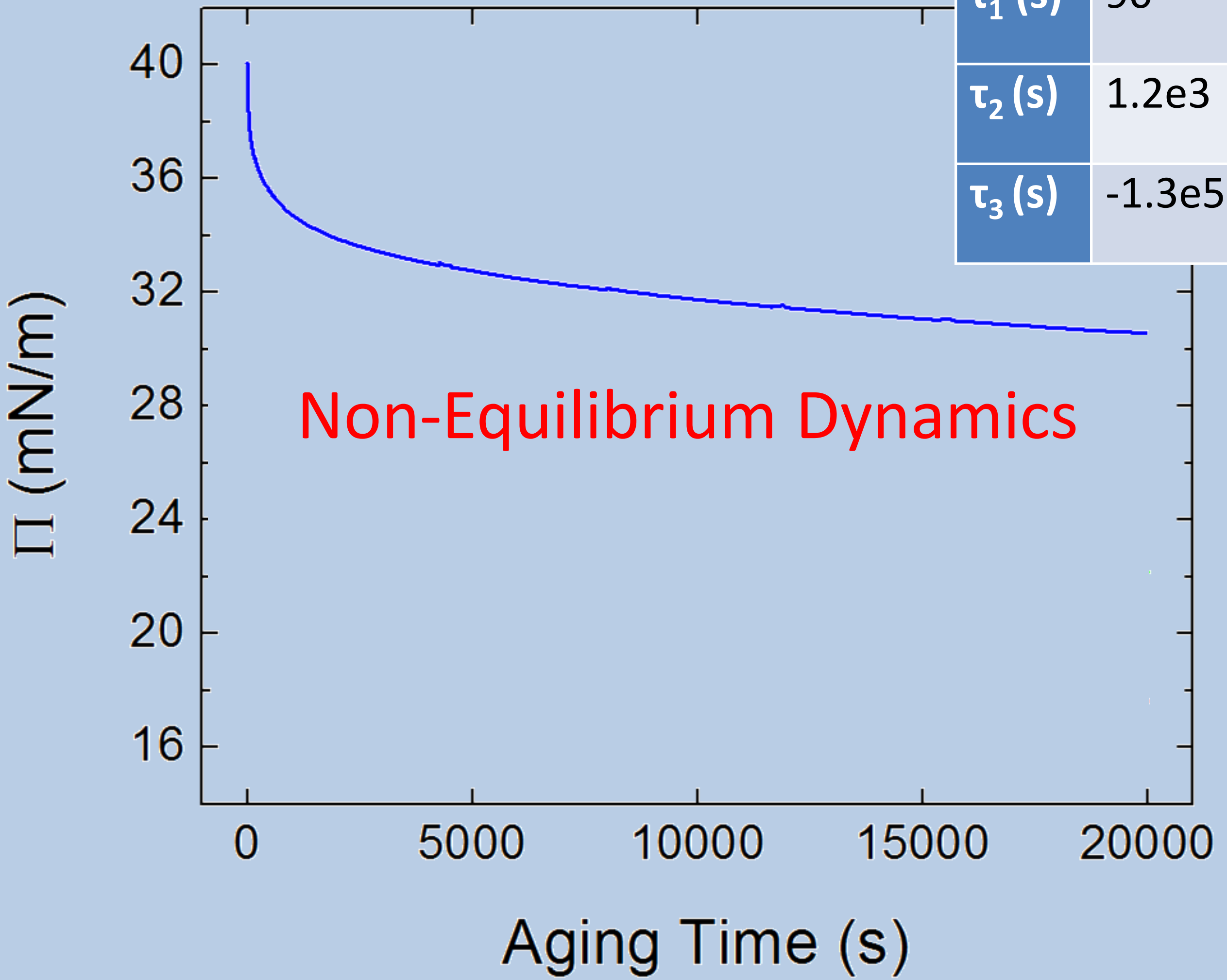
- Compress to specific surface area
- STOP compression (hold barrier in place)
- Measure diffusion of particles using XPCS for several hours
- Make new film
- Repeat for different surface area

Pressure Post-Compression

$$\Pi = ae^{-t/\tau_1} + be^{-t/\tau_2} + ce^{-t/\tau_3}.$$

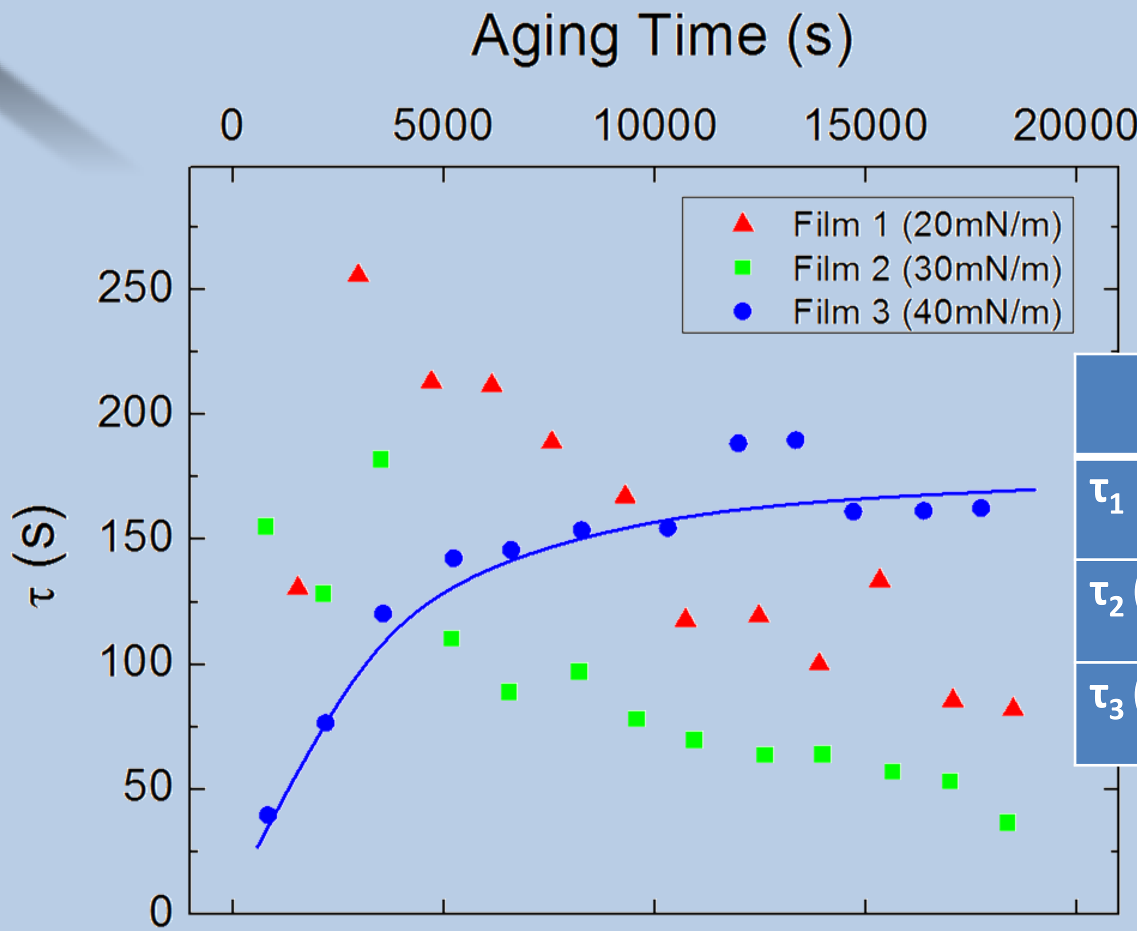
	Film 1	Film 2	Film 3
τ_1 (s)	90	60	160
τ_2 (s)	1.2e3	1.7e3	2.1e3
τ_3 (s)	-1.3e5	3.5e5	2.4e5

Things are moving: So what?



- Interparticle **spacing** changed by < 2Å (1%)
- Level of **disorder** varied by < 15%

Diffusion Timescales



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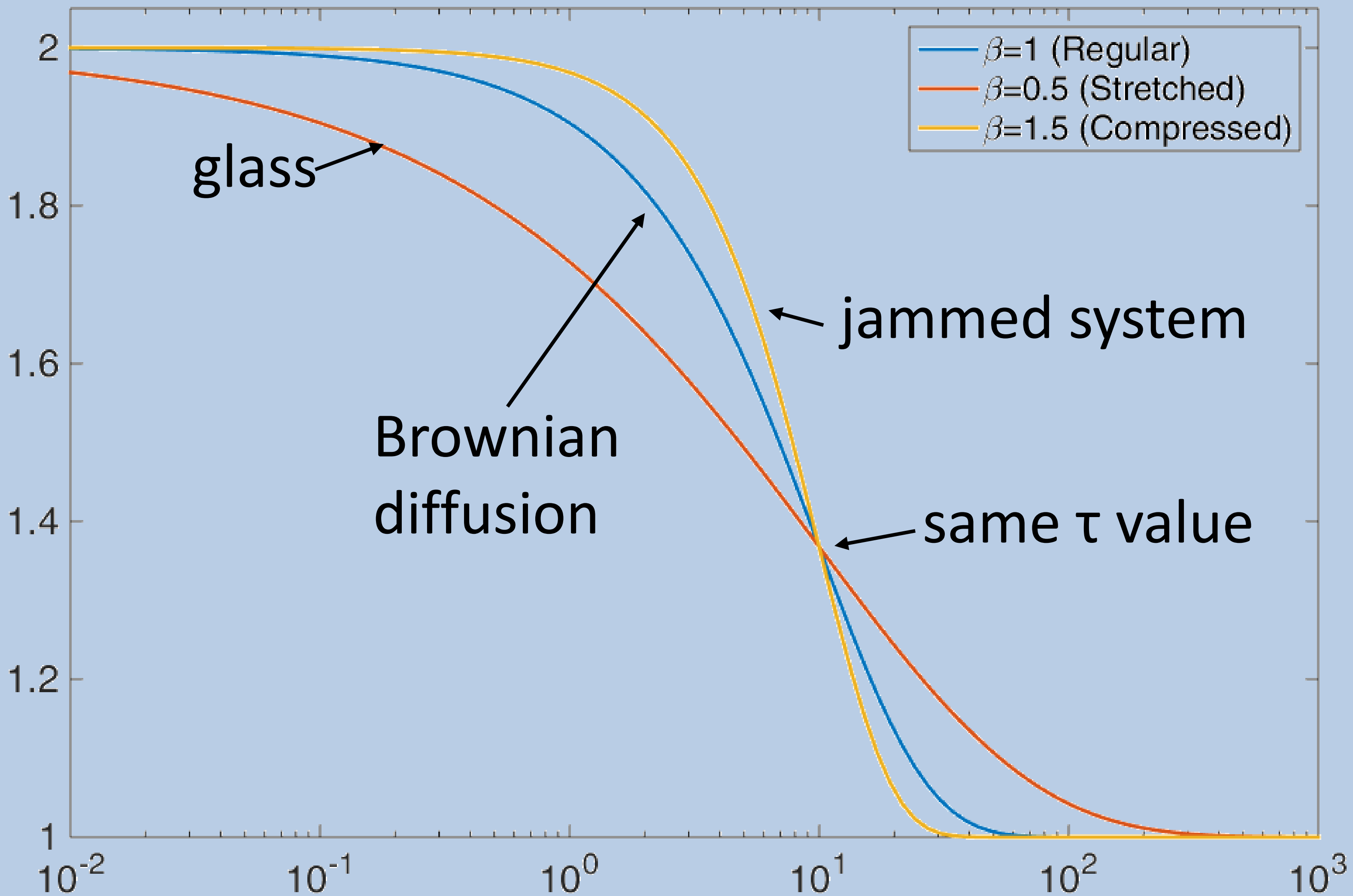
$$g_2(\Delta t) - 1 = b\left[Ae^{-\left(\frac{t}{\tau}\right)^{\boxed{\beta}}}\right]^2$$

Effect of Stretching Exponent



Jamming (colloquially)

Jamming (physics)

Jamming - an arrangement of particles undergoes structural arrest, transforming from a colloidal suspension into a disordered solid characterized by a yield stress, as the phase space no longer supports macroscopic motion.

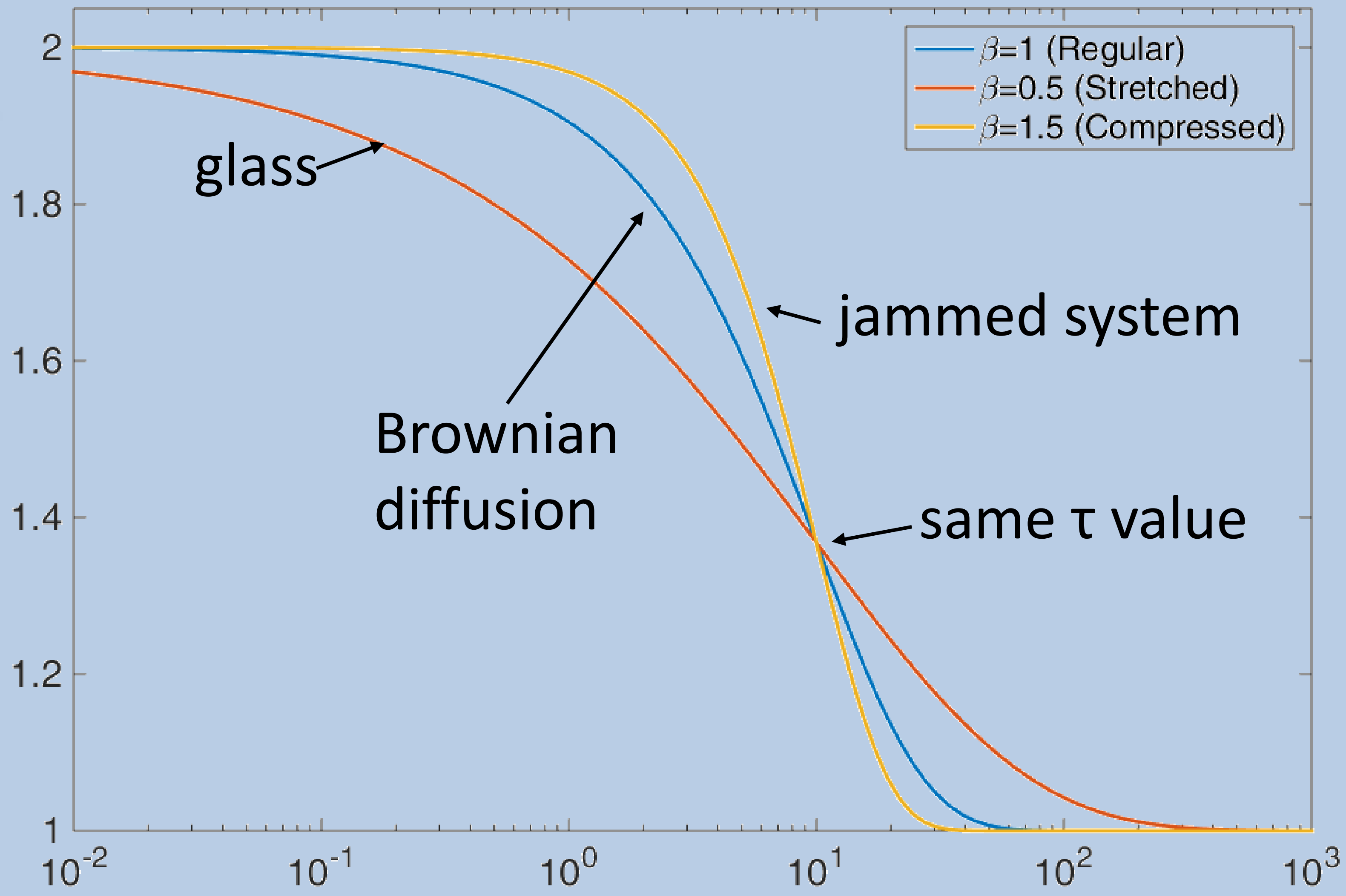
Glass transition – occurs with temperature

Jamming transition – occurs with density (pressure)

Examples:

- Sand
- Macaroni or rice
- Traffic jams

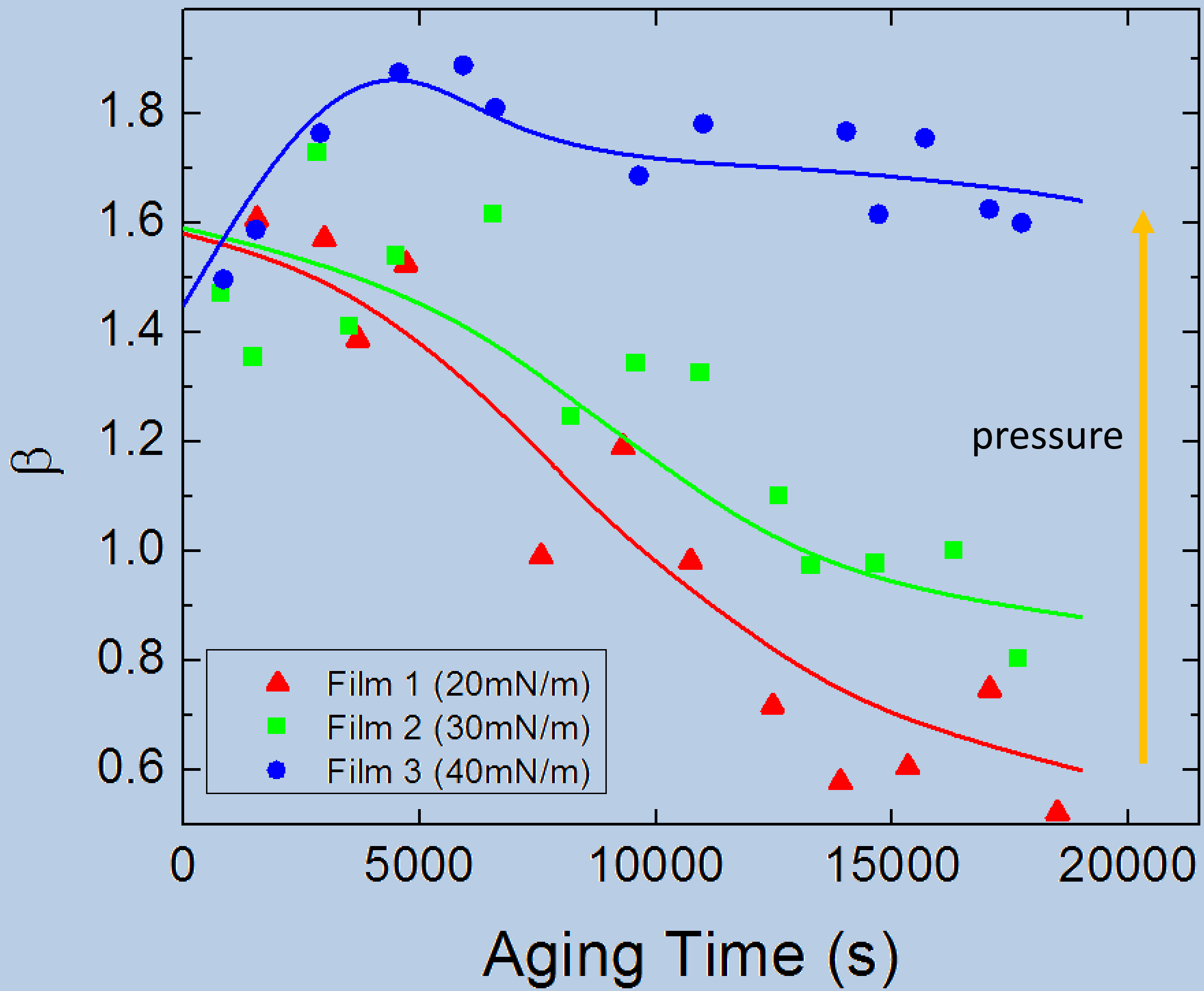
Effect of Stretching Exponent



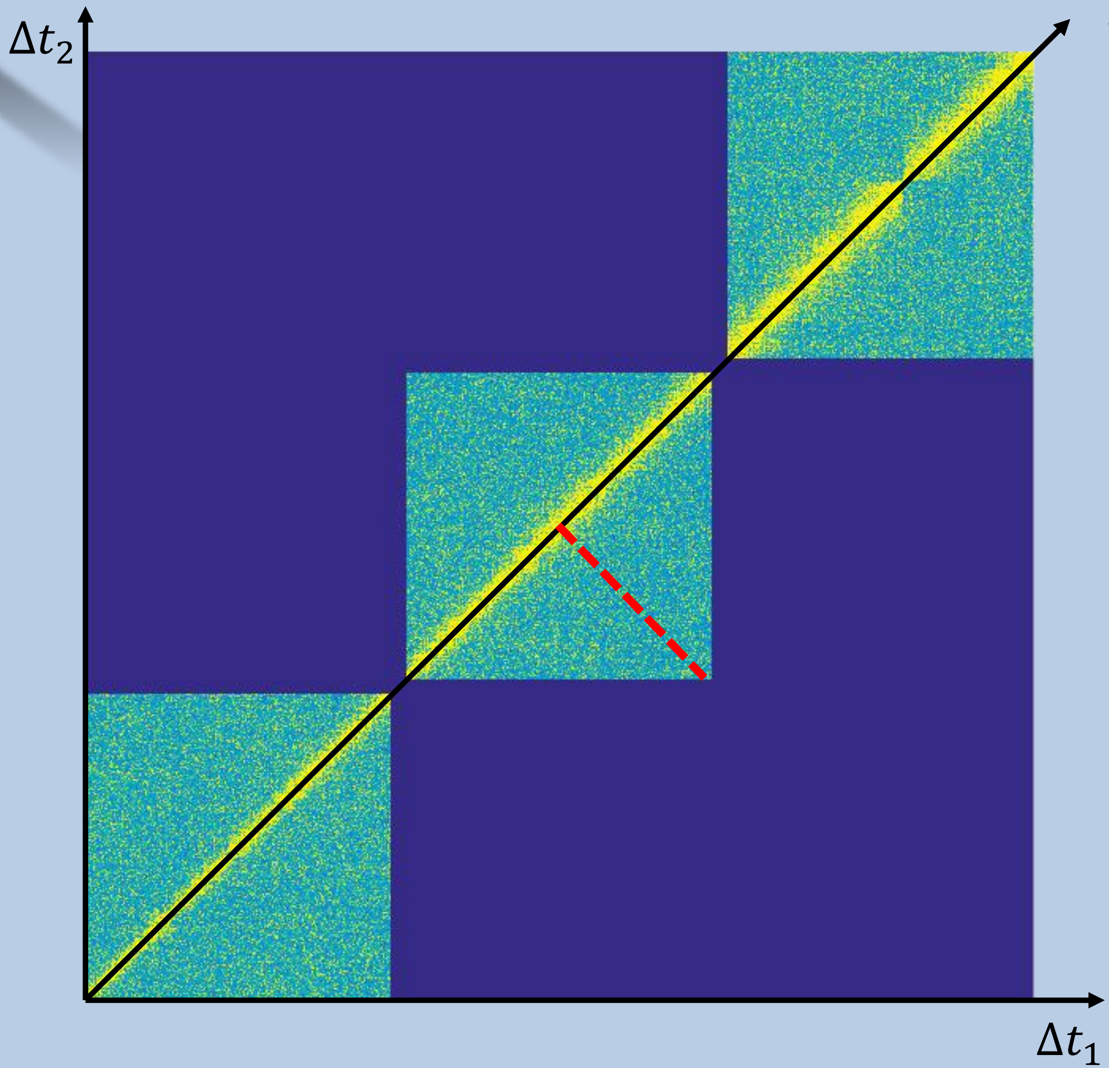
Avalanches in Jammed Systems

https://www.youtube.com/watch?v=5cgQoUMd-s4

Stretching Exponent



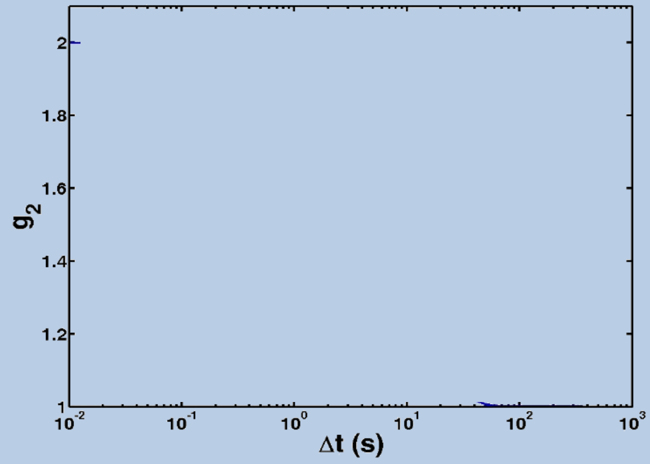
2-Time Autocorrelation



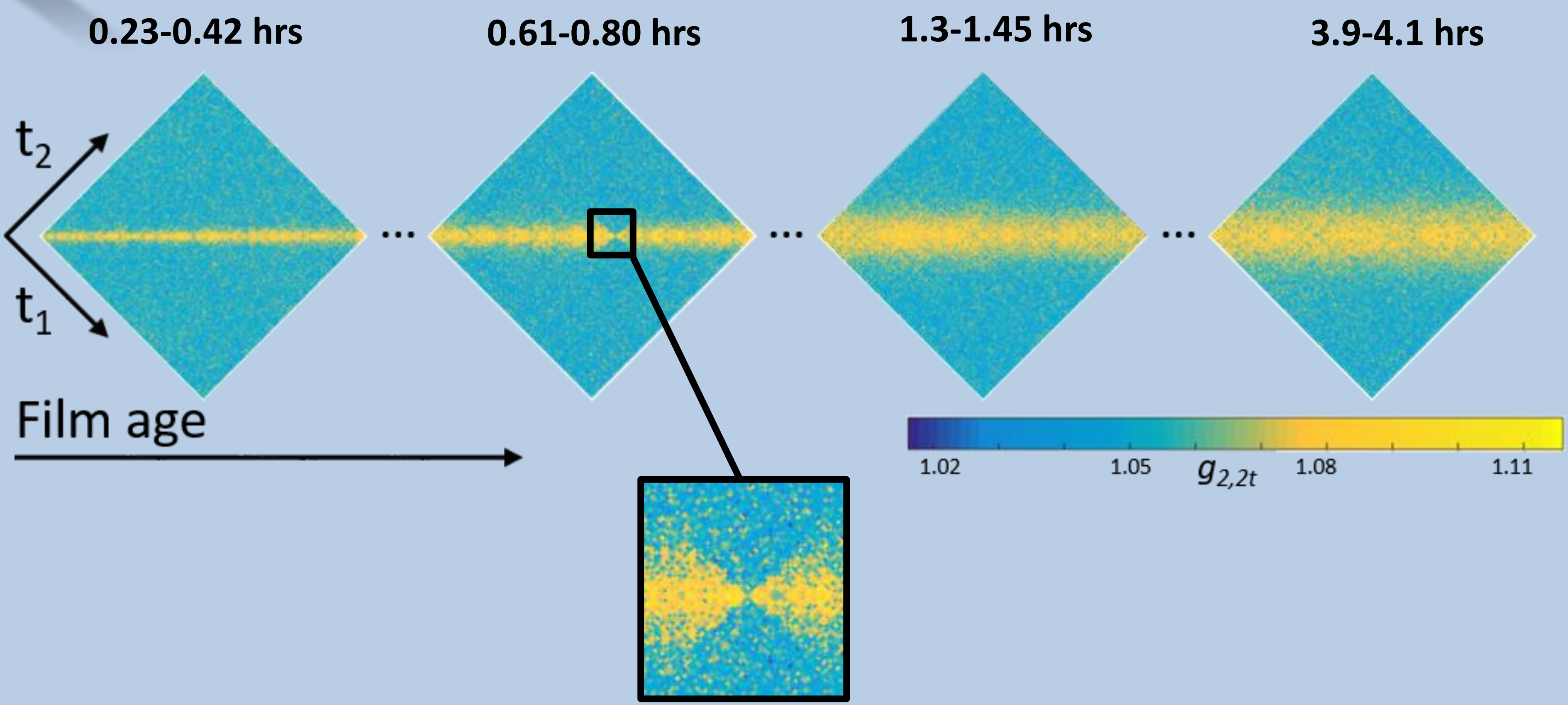
$$g_2(\Delta t) = \frac{\langle I(t) I(t+\Delta t)\rangle_t}{\langle I(t)\rangle_t{}^2}$$

$$g_{2,2-time}(\Delta t_1, \Delta t_2) =$$

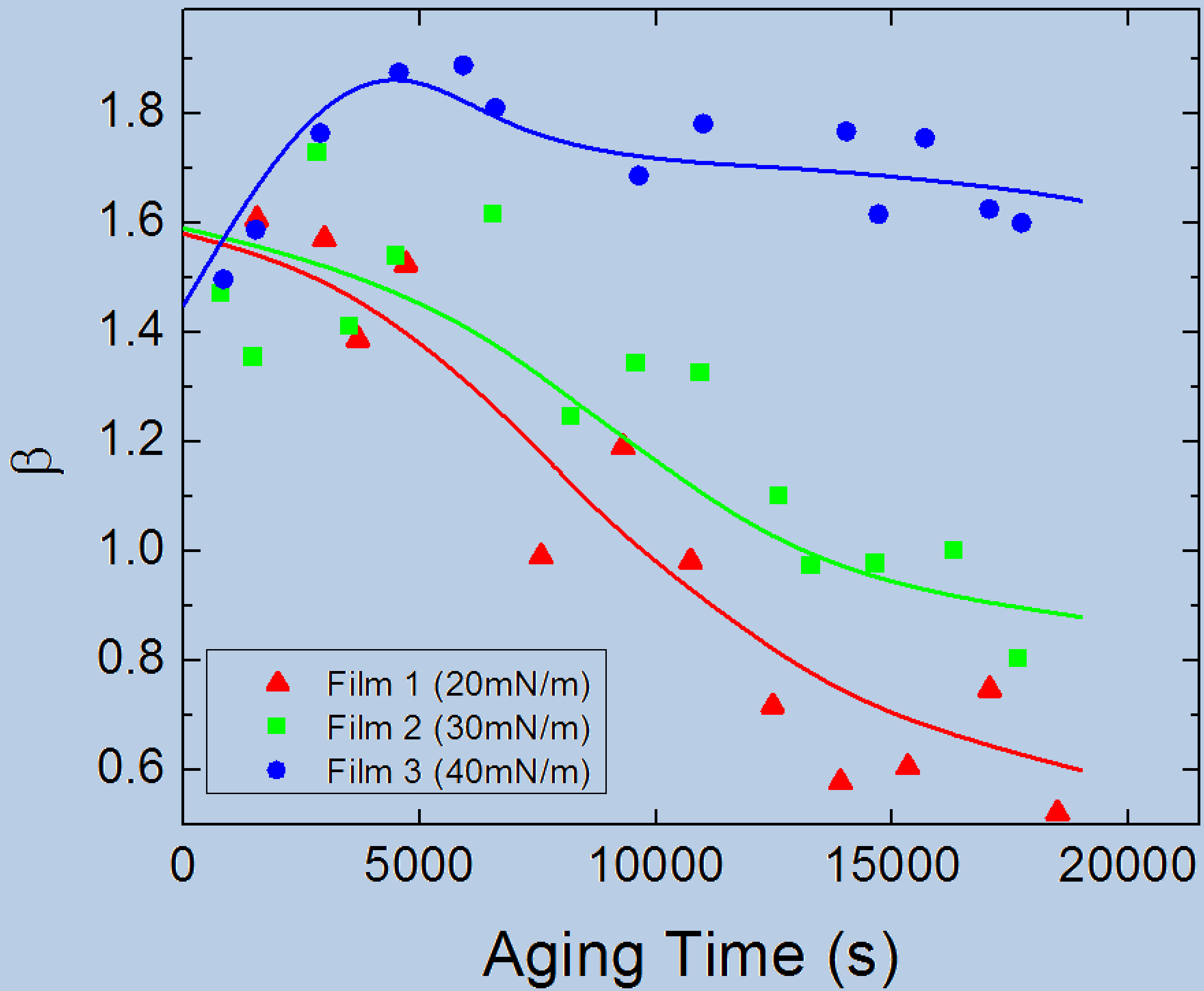
$$\frac{\langle I(t+\Delta t_1) I(t+\Delta t_2)\rangle_t}{\langle I(t)\rangle_t{}^2}$$



Avalanching



Pressure-Dependent Trends



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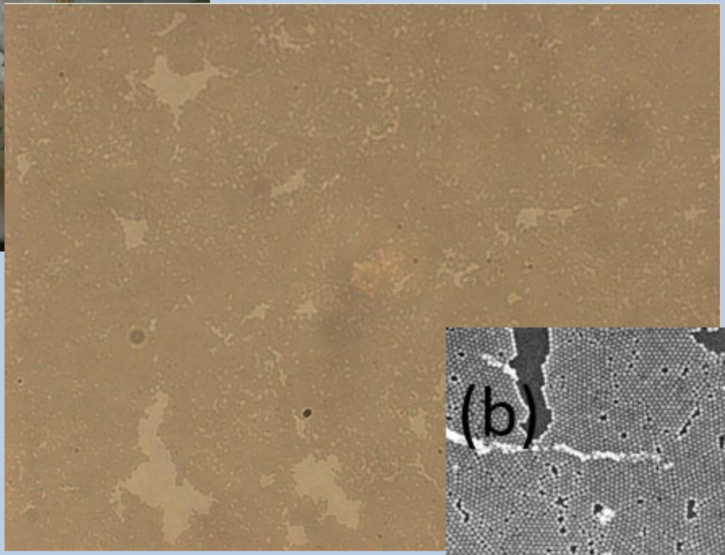
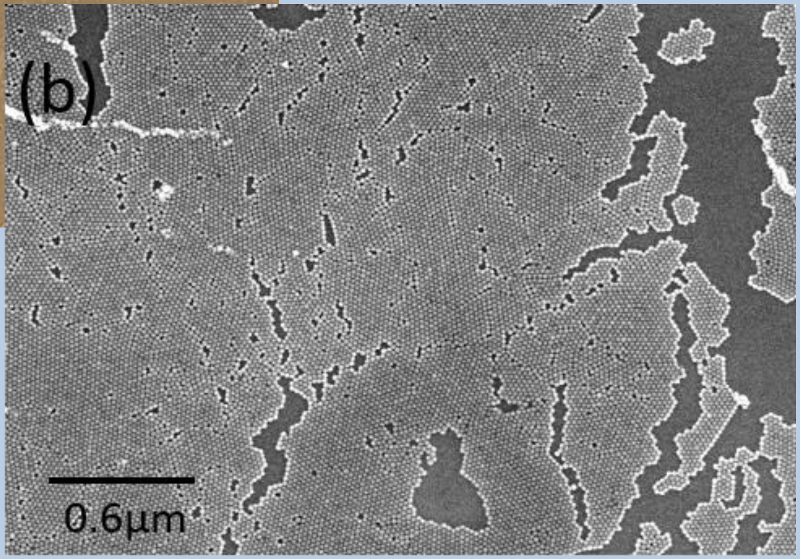




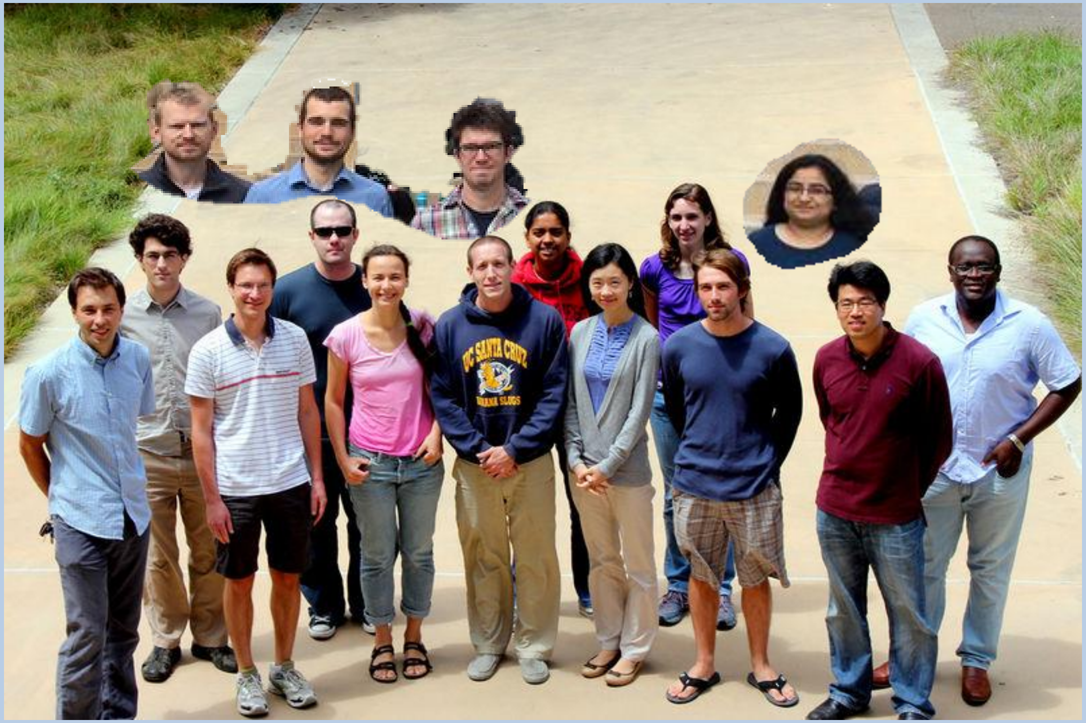
During aging:

- No change in interparticle spacing
- No change in disorder

- Jammed system
- Non-equilibrium dynamics
- Clear signs of aging

Acknowledgements

- Oleg Shpyrko
- **Jacob Stanley**
- Yeling Dai
- Sean You (U. Chicago)
- Chris Parzyck
- Jim Wingert
- Andrej Singer
- Binhua Lin (APS/S15/U Chicago)
- Mati Meron (APS/S15/U Chicago)
- Zhang Jiang (APS/S8)
- Suresh Narayanan (APS/S8)
- Alec Sandy (APS/S8)



UC San Diego

National Science Foundation
WHERE DISCOVERIES BEGIN

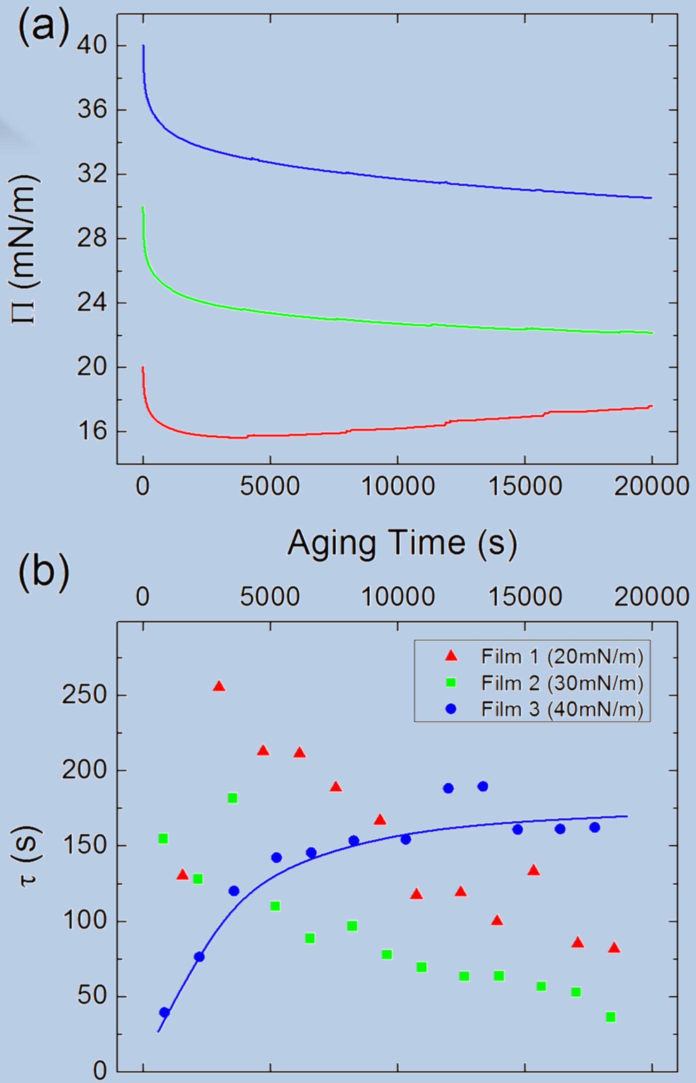
Apologies

“Call me when the bomb squad gets here, I want to take pictures for Oleg’s tenure file.” –Dimitri Basov, November 2012

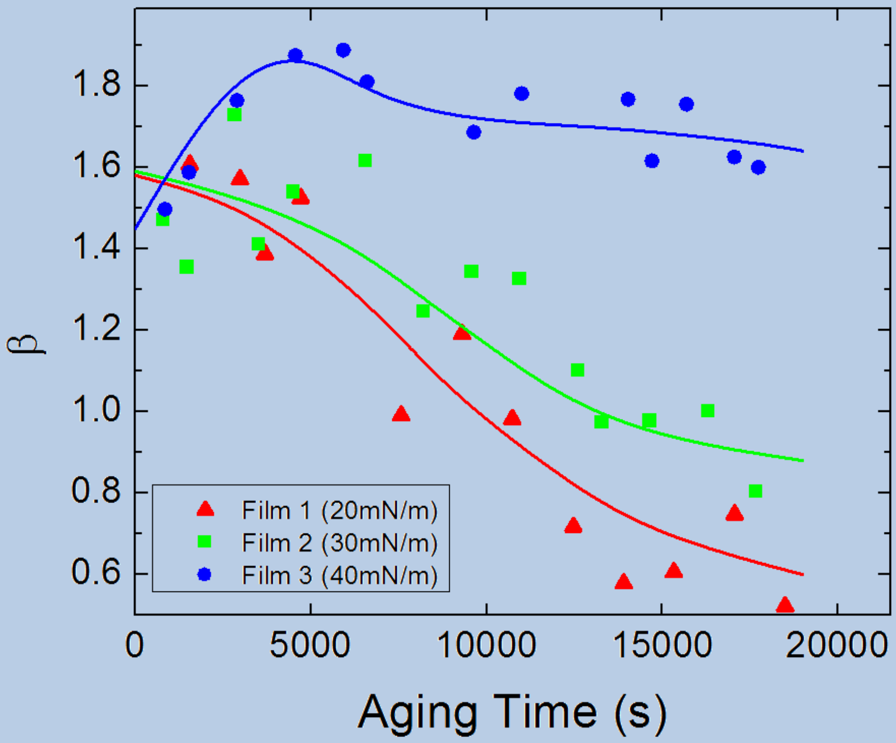
Thank You!

Backup Slides

Graphs

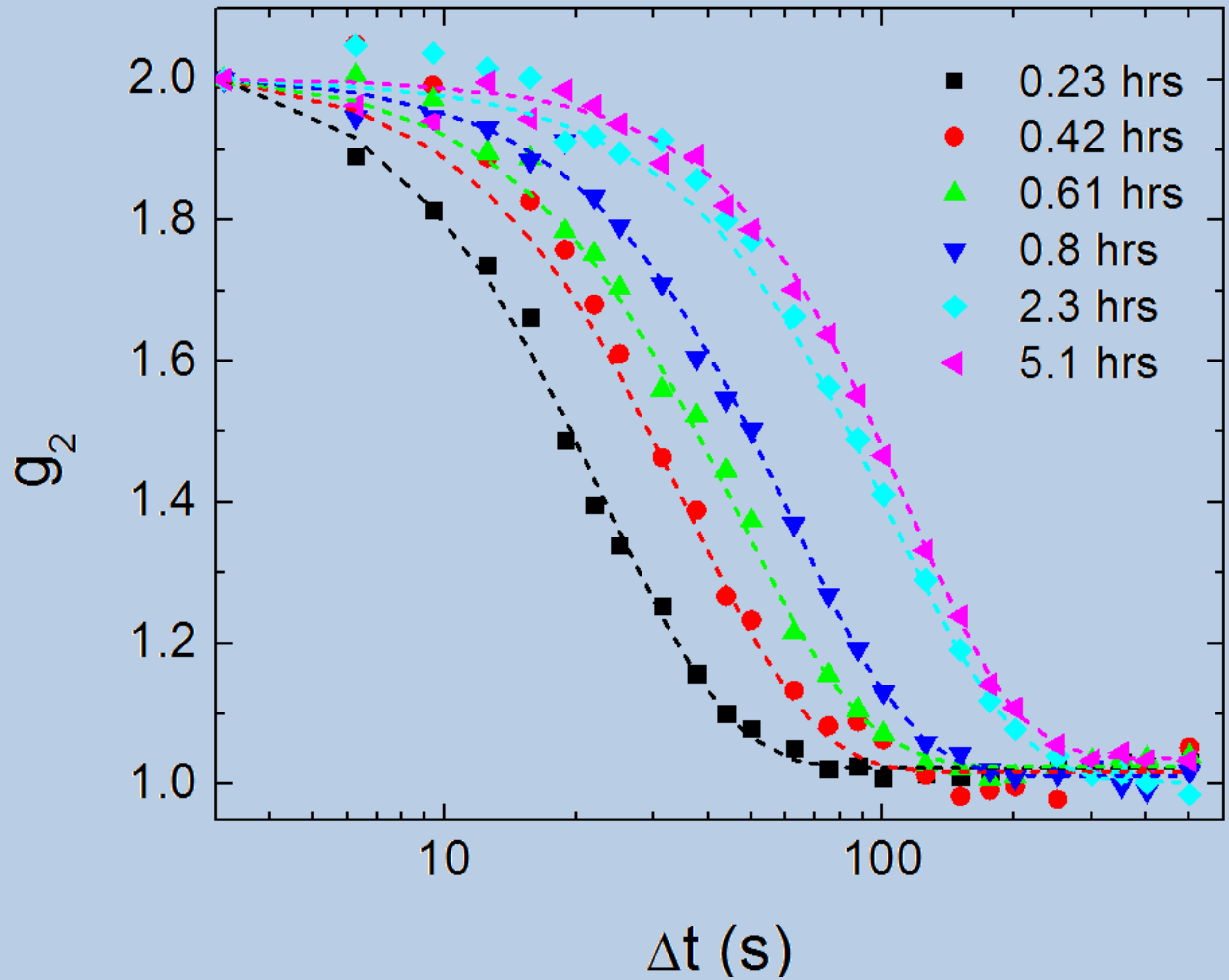


(a)
40
36
32
28
24
20
16
Π (mN/m)
0
5000
10000
15000
20000
Aging Time (s)
(b)
0
5000
10000
15000
20000
Film 1 (20mN/m)
Film 2 (30mN/m)
Film 3 (40mN/m)
250
200
150
100
50
0
τ (s)

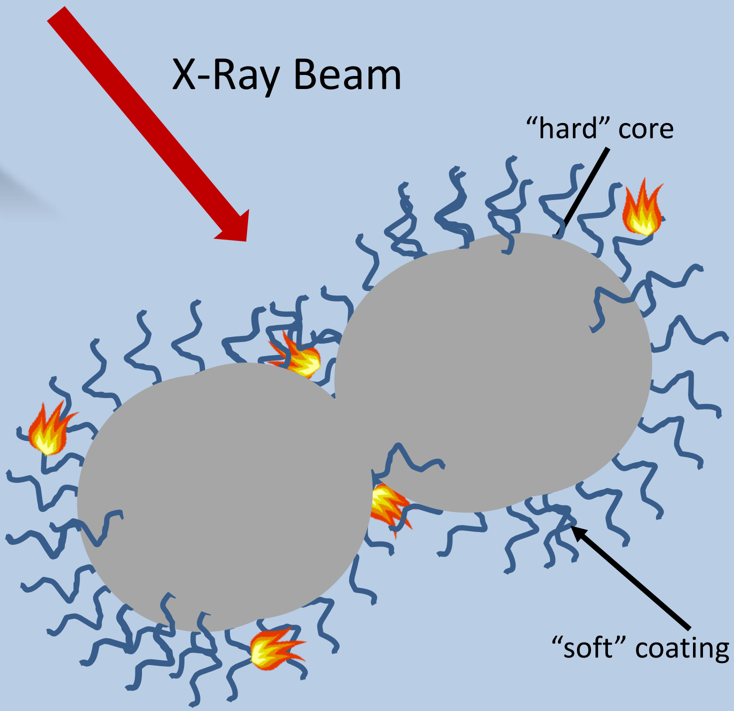


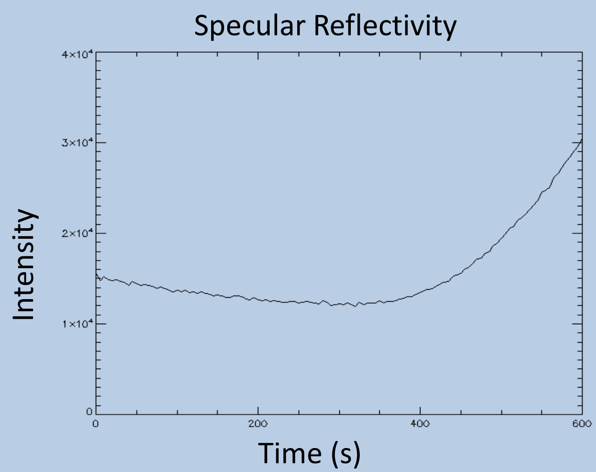
1.8
1.6
1.4
1.2
1.0
0.8
0.6
β
Film 1 (20mN/m)
Film 2 (30mN/m)
Film 3 (40mN/m)
0
5000
10000
15000
20000
Aging Time (s)

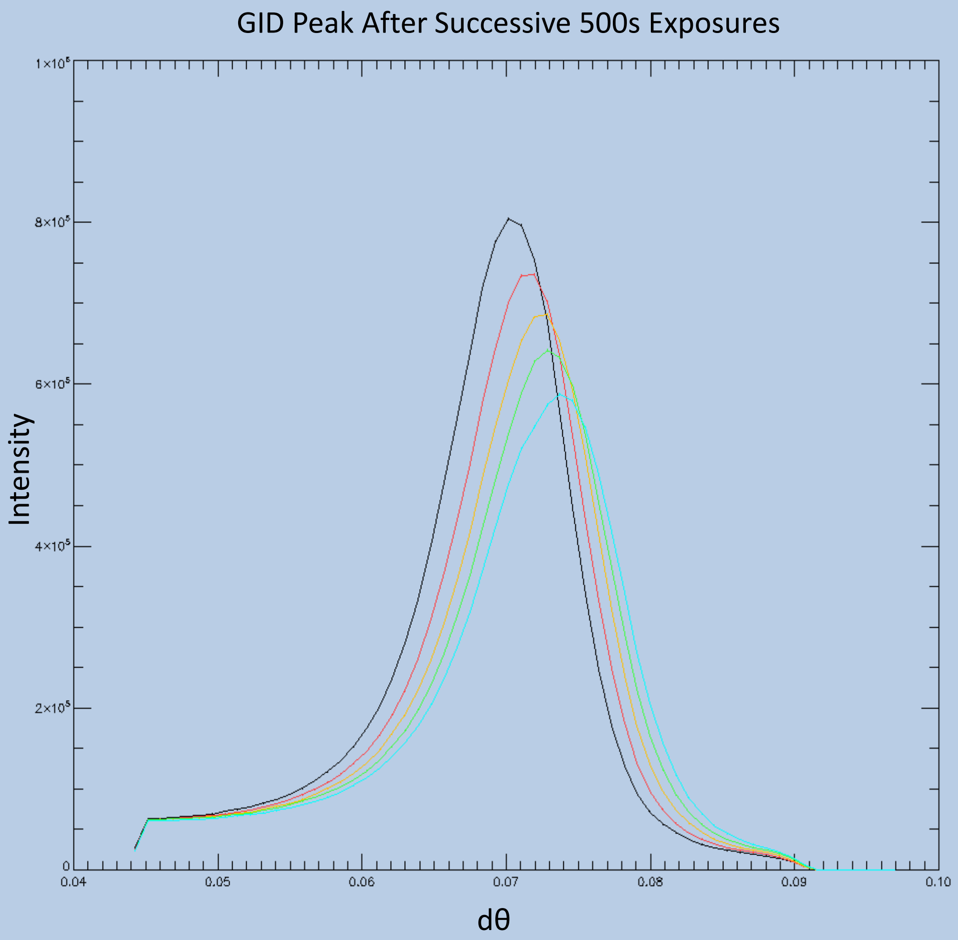
40mN Film Autocorrelation Curves



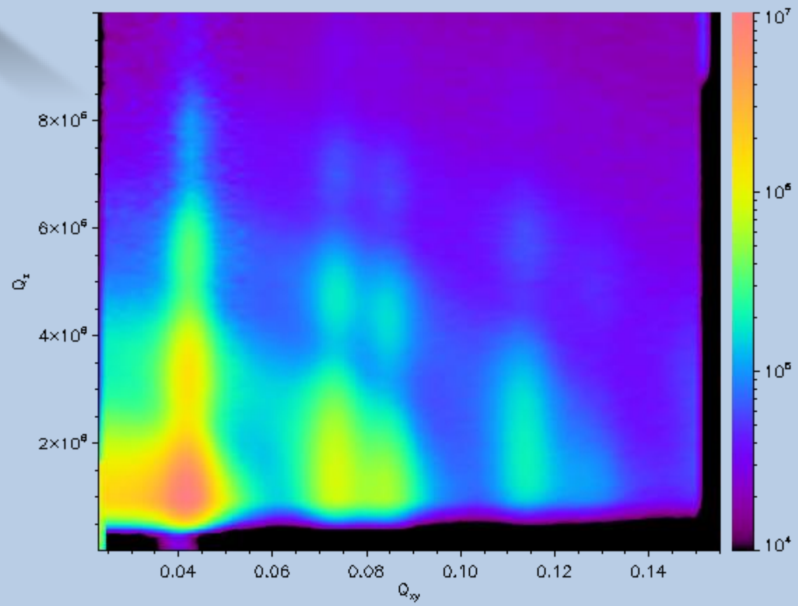
Radiation Damage

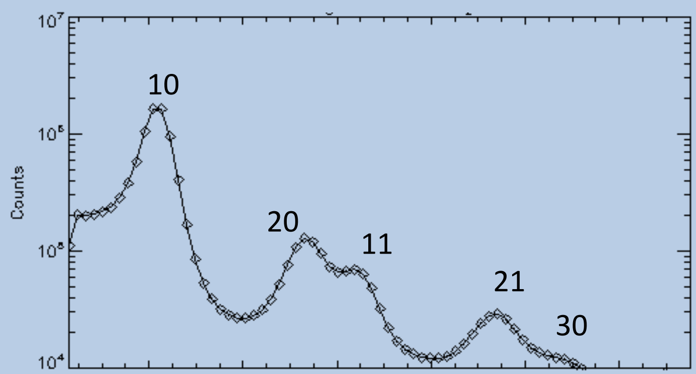


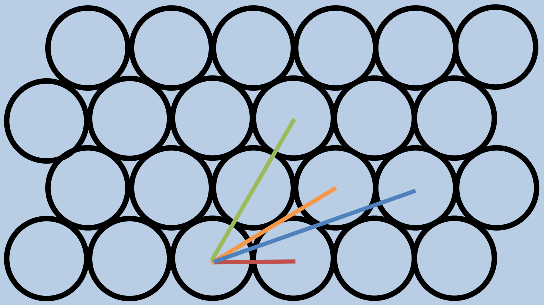




In-Plane Film Structure







Nearest Neighbor Spacing

	1st	2nd	3rd	4th
Hexagonal Close Packed	1	$\sqrt{3}$ ≈1.73	2	$\sqrt{7}$ ≈2.65
Experiment	1	1.75	2.01	2.74

Why Iron Oxide?